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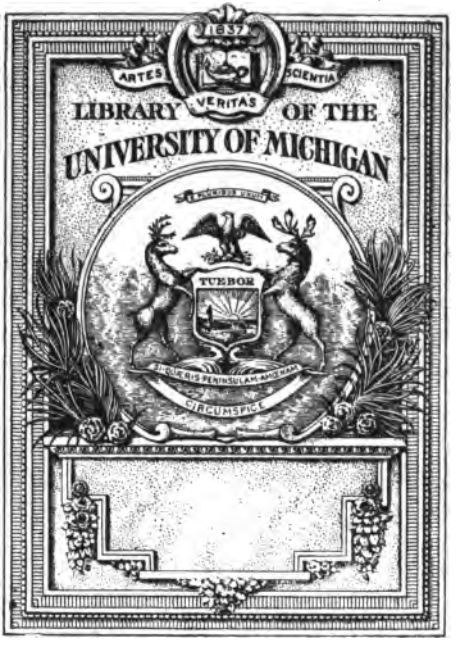

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SUMMIT OF MOUNT ETNA, 1783. (SPALLANZANI) *Frontispiece*

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MANUAL

OF THE

CHEMICAL ANALYSIS OF ROCKS

BY

HENRY S. WASHINGTON, Ph.D.

THIRD EDITION, REVISED AND ENLARGED

NEW YORK
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PREFACE TO THE THIRD EDITION

THE present edition has been thoroughly revised and considerably enlarged. Some changes in details of procedure have been introduced that were suggested by the equipment and facilities of a modern laboratory, as contrasted with those which served for the work upon which the previous editions were based. But the endeavor has been made to describe the various procedures so that they may be readily carried out by one working in a laboratory that is not provided with all possible facilities. Some new methods have been introduced, but it has been thought to be the wiser course to adhere to well-known and oft-tried reliable methods, rather than to supplant them by others more recently proposed, unless these have been tried and proved to be of undoubted superiority.

The various methods have been treated in much greater detail than in previous editions, and more stress has been laid on the sources of error both in operations and in methods; experience has shown that such discussions will be of service to the intelligent student, particularly if he is working alone. It is to be hoped that the many sources of error, and the many precautions, which have been enumerated, will not induce discouragement at the outset, but that they will, rather, serve to stimulate to greater and more active and intelligent interest in and understanding of the analysis of rocks.

Some of the most recent and standard text-books have been at my elbow during the revision. The work throughout is greatly indebted, as before, to the invaluable writings, as well as to the friendly advice, of Dr. W. F. Hillebrand; while the treatise of Dr. J. W. Mellor has also been of great assistance and has been constantly consulted.

It is a pleasure to express my obligations to Dr. Arthur L.

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Day, Director of the Geophysical Laboratory, for his permission to undertake this revision while a member of its staff; and I would also tender my thanks to Dr. E. G. Zies, of this laboratory, for much friendly and valuable criticism and counsel, as well as for his kindness in reading the proofs during my absence.

H. S. W.

Geophysical Laboratory,
Carnegie Institution of Washington,
June 30, 1918.

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PREFACE TO THE FIRST EDITION

THE object of this book is to present to chemists, petrologists, mining engineers and others who have not made a particular study of quantitative analysis, a selection of methods for the chemical analysis of silicate rocks, and especially those of igneous origin. While the publication of such a work may seem superfluous in view of the existence of Hillebrand's treatise on this special topic, yet justification may be found in the fact that the latter is intended, not so much for one who is not very conversant with the subject, as for the practiced analyst, to whom it is an indispensable guide.

A further reason for its appearance is that, apart from Hillebrand's book and a paper by Dittrich, there does not seem to exist any separate modern treatise on the chemical analysis of rocks. The space devoted to this branch of analysis in the text-books is usually very small, and the various methods are widely scattered and often inadequately described. This is especially true in regard to the minutiæ of manipulation and precautions to be observed, and to the determination of elements which, though usually accounted rare, have of late years been shown to be very common rock constituents. This neglect is rather striking in view of the prominence given in the last decade or so to the chemical composition of igneous rocks.

There is an increasing number of geologists, petrologists, chemists and others, who are desirous of making chemical analyses of rocks, but who have had little or no experience in the subject, except that gained in the ordinary course of quantitative analysis, in which the study of silicates is usually confined to the examination of a feldspar or some such simple mineral. It is for the benefit of this class of students that the present book is written. The general plan adopted therefore is, not to attempt a complete treatise on rock analysis, but to present only

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certain methods which have proved simple and reliable in the experience of the chemists of the U. S. Geological Survey and of my own. The more important of these, and some of the principal operations, are described with great explicitness. Many small details of manipulation are gone into which are omitted by Hillebrand and the text-books as unnecessary, a knowledge of them being either presupposed or their demonstration left to the instructor.

In this way it is hoped that it will be possible for an intelligent student, with some knowledge of chemistry and a little analytical training, to be able to complete a satisfactory analysis of an ordinary silicate rock, without personal instruction and after comparatively short practice. To the expert analyst, therefore, the book will contain much that is superfluous, but for this no apology is offered. What are superfluities to him will, it is hoped, be welcome to the novice.

It is assumed that silicate igneous rocks will be the most frequent objects of investigation. At the same time, the methods described serve equally well for most silicate metamorphic and sedimentary rocks. Such rocks as saline deposits, coals and others containing organic matter are not considered. The methods are not generally adapted to the analysis of ores which, with such constituents as sulphides, arsenides and other compounds of the heavy metals, often call for different and more complex means of separation than are here given. The same is true of many minerals, though the methods found in the following pages are those appropriate to the analysis of most silicates. The analysis of meteorites also demands the employment of special methods, and in most cases these bodies are of such character that their examination should not be undertaken by the inexperienced, especially if only a limited supply of material is available.

The methods selected are, in general, those adopted by the chemists of the U. S. Geological Survey, and which in their essentials I have employed in my own scientific work for a number of years. Some modifications have been made, chiefly in the direction of simplification and the elimination of certain refinements which do not seem called for when the object of the volume is considered. There is no attempt at the introduction of new methods or the description of alternative ones which, either on

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theoretical grounds or on account of practical difficulties, are deemed to be less well adapted to the needs of students than those which are here given. Theoretical discussion will be limited to what may seem necessary to make clear the principles of certain methods or the reasons for their selection.

I have also endeavored to point out to the student the importance of chemical analyses for the study of rocks, and their possible bearing on some of the broad problems which form the objects of the science of petrology. In other words, it has been sought to emphasize the fact that petrographical classifications and the study of textures and of minerals in thin sections are not the sole aims of the science, but that, supplemented by a knowledge of the chemical composition of igneous rocks, they are only means to broader ends. I can only express the hope that this little book will aid in the progress of petrology, by leading to an increase in the knowledge of chemical analysis among petrologists and rendering our data in the way of rock analyses of superior quality more numerous.

The great obligations under which I am to Dr. Hillebrand's work are evident throughout and are most gratefully acknowledged. The text-books of Fresenius, Classen, Treadwell, and Jannasch have also been consulted, and the book is indebted to them in many ways. It is also a pleasure to express my obligations to several friends for valuable advice and assistance, and especially to Prof. S. L. Penfield and Prof. L. V. Pirsson, to whom my first knowledge of, and training in, quantitative analysis are due. A number of most useful hints in manipulation were learned from these two analysts, all of which could not be specifically mentioned in their proper places, but which are acknowledged here. Acknowledgments are also due to the Trustees of the Carnegie Institution for permission to publish an analysis made under their auspices.

The factors used in calculations are those given by Cohn in his recent translation of Fresenius' Quantitative Analysis. All temperatures are given in centigrade degrees. The metric system is used generally, except in dealing with such pieces of apparatus as are usually sold in this country on the basis of English measurements.

HENRY S. WASHINGTON.

LOCUST, N. J., May, 1904.

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THE CHEMICAL ANALYSIS OF ROCKS

PART I

INTRODUCTION

1. Importance of Chemical Analyses

For the greater part of a century, since their study began, igneous rocks were regarded almost solely as more or less fortuitous mineral aggregates, these being usually assumed to be due to the fusion of previously existent rock bodies or to the mixture of several igneous magmas. With the introduction of the microscope, a more intimate study of their field relations, and especially with the improved chemical methods and the greatly increased number of satisfactory chemical analyses of the last thirty years, a decided change has come about in the way of regarding them.

Various observations and theories of the order of succession and of crystallization of minerals, differentiation of bodies of magma, consanguinity and petrographic provinces, have been made and advanced, and the principles of physical chemistry have been applied to their study; all these tending to throw light on the origin, genetic relationships and mode of formation of igneous rocks. Briefly put, the tendency of the modern study of igneous rocks is toward considering them as falling under Spencer's law of evolution; that is, in the general line of passage from "an indefinite incoherent homogeneity to a definite, coherent heterogeneity." In other words, the petrologist of the present day does not regard them as merely solidified mineral aggregates, whose characters are largely the result of chance conditions, but as bodies which are the result of the action of physico-chemical proc-

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esses, and whose characters are determined by evolutionary laws. It is the aim of petrology to interpret these pieces of evidence and to ascertain the laws which govern the origin and formation of rocks. It is needless to say that this modern point of view renders igneous rocks objects of far greater scientific interest than they could have been under the older one.

For the proper study and understanding of these theoretical aspects of igneous rocks, the knowledge and application of some of the principles of physical chemistry are necessary, and it is obvious that for this a detailed knowledge of their chemical composition, as well as of their field relations, is essential. Conversely, it seems probable that the study of igneous rocks will be of service to the sister science of physical chemistry, since the petrologist is dealing with solidified solutions which have been formed and acted on by physico-chemical forces, under conditions of temperature, pressure, and mass which it is now impossible to reproduce in the laboratory.

To the petrographer, who deals especially with the descriptive and systematic portions of the science of rocks, the chemical analysis of igneous rocks is assuming each year an increasing importance for their classification. Whether this is based only on the inherent characters of the rock-mass itself, or whether it takes account of genetic relationships, the chemical composition is becoming more and more an essential factor, and one which can no longer be relegated to the background, behind the superficially more prominent features of mode of occurrence, texture, and qualitative mineral composition.

While our knowledge of metamorphic rocks is, as yet, not so far advanced as that of the igneous ones, chemical composition plays, likewise, a most important part in their study and classification, and, to a certain extent, the same is true of the sedimentary rocks.

As regards the economic side of geology, such as the origin and formation of ores and useful mineral deposits, there is accumulating evidence of the importance of a knowledge of the chemical composition of igneous and metamorphic rocks. This refers not only to their main features, but also to the occurrence in them of the less abundant elements, which by certain processes of segregation may become commercially available.

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It is therefore evident that we possess in chemical analysis a means of investigation that complements, and is of value fully commensurate with, the study of rocks in the field or with the microscope. That this is generally recognized is shown by the increasing prominence given to chemical analyses in recent petrological and petrographical papers, as well as in publications of an economic character. It is also shown by the attention given to this study by official organizations, and by the growing number of those who make, or who desire to make, analyses of rocks.

2. General Character of Analyses [1]

For a fuller understanding of the general subject, it will be well to discuss briefly the factors which make up the character of a rock analysis, and which determine its value.

The fulfilment of two conditions is essential to the value of a rock analysis: the specimen analyzed must be representative of the rock-mass, and the analysis itself must truly represent the composition of the specimen selected. The more closely both of these conditions are met, the greater will be the value of the analysis.

The representative character of the specimen is determined by the character of the rock-mass, as influencing both its selection and the amount of material taken for analysis. These points will be discussed subsequently (p. 58).

Assuming that the sample is representative of the rock-mass, the degree of correspondence between the figures yielded by the analysis and the real chemical composition of the rock is dependent on the two factors of accuracy and completeness.

Accuracy of Analyses.—By accuracy is meant the degree of precision with which the constituents sought for are determined, quite apart from whether or not all of those present have been determined or separated from one another. The accuracy of an analysis is dependent upon the methods used and upon the ability of the analyst to execute the various processes successfully. The purity of the reagents and the adequacy of the apparatus are also factors.

[1] This and the next two sections are a somewhat summarized statement of part of the discussion published in Prof. Paper U. S. Geological Survey, 99, pp. 10–18, 1917.

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It must be borne in mind that no method is capable of yielding results of absolute accuracy, any more than it is possible to construct a mathematically exact geometrical figure. Certain sources of error are inherent in all, some of a general nature, and others of a character dependent upon the method employed. The analyst must rest content with reducing these to a minimum, by selecting methods which have been shown to be reliable. In this we cannot do better than follow the chemists of the U. S. Geological Survey, whose experience is of the widest, and who have set up a standard of analytical methods and practice for rocks and minerals that is beyond all others.

But the selection of proper methods is not the only desideratum. They must be carried out in a proper way, which will not lead to errors of a purely mechanical kind that may easily vitiate the results of the theoretically most accurate method. In this matter the analyst himself is the most important factor. He should have, not only sufficient knowledge of the facts of chemistry and of the principles of analysis to work understandingly, but also the dexterity and manipulative skill to enable him to carry out the various processes successfully. While it may be true of some analysts that, like poets, they are born, not made, yet granted intelligence and chemical knowledge and a fair amount of dexterity and application, the necessary manipulative skill will come with practice, often in a surprisingly short time.

The analyst should beware of falling into careless habits or of allowing the analysis to become merely routine work. Carelessness is as fatal to obtaining good results as poor methods or impure reagents. During the whole progress of an analysis attention should be paid to every point of theory or manipulation, the influence of the various conditions or constituents should be considered, and indeed the analysis should be carried out from beginning to end with intelligent interest. This will turn into a pleasure what would otherwise be a dull and monotonous succession of precipitations, filtrations, ignitions and weighings, which, as has been justly said, is not chemical analysis.

That conscientiousness, a strict regard for the truth, and a firm determination to accept no result of doubtful character, are essential to the analyst goes without saying.

It may be said that the analysis of rocks (and minerals) would

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seem to be especially suitable for women; whose characteristics of neatness, patience, application, care and conscientiousness, and attention to detail, would be most valuable in analytical work. I know of but three women who have made any considerable number of rock analyses, and have found the work of all to be uniformly good.[1]

Completeness of Analyses.—As regards completeness, the ideal analysis should show the percentage of every constituent in the rock as well as the absence of such whose presence might have been expected on the basis of previous experience. This is not always attainable, and for practical purposes the analysis should give figures for all constituents which are present in sufficient amount to make their determination a matter of interest, or whose presence or absence may bear on the problem for which the analysis is made.

The number of constituents which should be sought for and determined depends, of course, very largely on the character of the rock. Thus, in most granites, quartz-porphyries and rhyolites which are of simple composition, comparatively few constituents need be determined to make the analysis satisfactory. On the other hand, in such rocks as nephelite-syenites, diorites, basalts, and tephrites, the number of constituents which should be determined is larger, and may easily reach twenty or more.

It is to be borne in mind that neglect to seek for some of the rarer constituents may lead to the overlooking of important features, and that an analysis complete as to the subsidiary constituents may be of great value in the future, even if this degree of completeness is not necessary for the end immediately in view. The analyst should turn out, and the petrologist should be willing to accept, only results of the highest character; so that it follows, as a general thing, that every analysis should be as complete as it is possible to make it.

The details of the constituents to be determined will be taken up later (p. 7), but it may be stated here in a general way that all the main constituents must be determined in every analysis, as well as those minor ones which enter into the composition of minerals that are present in notable amount. If the general character of the petrographical province or the microscopical examina-

[1] Cf. Washington, Prof. Paper, 99, p. 23.

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tion indicates the presence of certain of the rarer elements, these should also be looked for.

3. Microscopical Examination

The chemical analysis should always be preceded by a microscopical examination by the petrographer of the rock in thin section. There are several reasons for this. In the first place, by a comparison of several specimens in thin section one is able to judge, better than by a merely megascopic examination, whether the specimen selected for analysis may be considered as really a representative one. It has happened more than once that specimens selected for analysis without such microscopic study have been shown later to be abnormal forms and not typical of the rock mass or volcano under investigation; or else that several analyses have been made of one kind of rock, while equally important kinds have not been analyzed.

The microscope also frequently gives important indications as to the presence of rare constituents which should be determined, or the absence of others which may therefore be neglected. It will thus often prevent the overlooking of constituents the determination of which may be of considerable importance, or, on the other hand, may save much labor and time to the analyst in searching for substances which are not present, at least in determinable amount.

Thus, if microscopic zircons are present in a granite, the amount of zirconia should be determined to render the analysis satisfactorily complete, while if these are absent this substance can be neglected without serious diminution in the value of the analysis. The presence of crystals of a colorless, isotropic mineral, of low refractive index, will necessitate the determination of Cl and SO_3, as they may be crystals of colorless sodalite or haüyne, while if none are found under the microscope in a holocrystalline rock these constituents may usually be considered as absent.

Finally, the thin section will show much more definitely than the hand specimen whether the rock is fresh and unaltered enough to justify its analysis.

It should also be noted that the percentage amount of certain constituents may sometimes be determined by the microscope with almost as much accuracy as by chemical analysis, and often

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with greater ease and expedition. This will be true for some which are present only in very small amounts and which occur in minerals of definite composition.

Thus, if zirconia is present only in zircon, or fluorine in fluorite, or sulphur in pyrite, the amount of these minerals in the rock can be readily estimated by Rosiwal's method,[1] and the percentage of ZrO_2, F, or S, respectively, may be easily calculated. Though this method also applies to phosphorus pentoxide in apatite, yet this substance is of such importance as a minor constituent, and its determination analytically is so easy and expeditious, that its amount should always be ascertained in the regular analytical way. Except possibly for fluorine existing only in fluorite, this microscopical method is, however, less satisfactory than the chemical, and if it is adopted, a note to that effect should be made in the statement of the analysis.

4. Constituents to be Determined

Importance of Completeness.—In the earlier days of petrography, the petrographer was quite content if the analyst reported figures for only eight or nine constituents, and he did not always insist on the separation of the two oxides of iron. One seldom meets with analyses of this period in which TiO_2 or P_2O_5 are mentioned, to say nothing of such substances as ZrO_2, BaO or F. In the absence of exact knowledge of the mineral composition of rocks the presence of such rare elements was not often suspected, nor did neglect of them in the course of the analysis necessarily cause such low summations as to give rise to suspicions that something had been overlooked. This was partly because these rarer elements almost invariably occur in very small amounts, partly because some of them, as TiO_2, P_2O_5, ZrO_2, Cr_2O_3 and SrO, are precipitated and weighed with other constituents, and partly because the analyst of those days was not as accurate in his methods as at present, and was content with a summation which would cause the rejection or the doing over of the analysis by a modern chemist.

After it became possible to study rocks in thin section, and when

[1] Rosiwal, Verh. Wien. Geol. Reichs-Anst., **32**, p. 143, 1898. Cf. Cross, Iddings, Pirsson, and Washington, Quant. Class. Igneous Rocks, Chicago, 1903, p. 204.

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the use of heavy solutions made the separation of the component minerals easy, it was found that the number of chemical constituents commonly present in rocks was far larger than had been supposed, although the importance of determining them was not recognized for many years. With improvement in old methods and the adoption of new ones, the determination of these minor constituents was greatly facilitated, and at the present day analyses in which figures are reported for twenty or more constituents are common, at least in some countries; though, unfortunately, there is still a tendency among many chemists to rest content with the determination of only the more notable ingredients.

At first sight it may not seem worth while to pay attention to constituents which are present in amounts only up to a few tenths of a per cent. But there are very good reasons for not neglecting them.

For one thing the determination or non-determination of some of them affects, and may affect seriously, the figures for other and more important constituents. This is because several of them are precipitated and weighed together, and then all except one are determined separately, so that the figure for the final one depends on those of the others, since it is determined by difference.

Thus, Al_2O_3, Fe_2O_3, Cr_2O_3, V_2O_3, TiO_2, ZrO_2, P_2O_5, MnO, and a little SiO_2 are thrown down and weighed together, all except the first are determined separately, and the weight of the Al_2O_3, which is usually greater than all the others combined, is ascertained from the difference. It is evident that if any one of the other oxides is neglected the figure for alumina will be too high, and this error may be serious. Similar cases are those of CaO and SrO and of P_2O_5 and V_2O_5, though in these the error involved will seldom be of great moment.

Again, the non-determination of such constituents as are not precipitated and weighed with others, will lower the summation of the analysis. This lowering may amount to so much as to cause an otherwise superior analysis to appear to be inferior.[1] Such non-determinations are those of H_2O, CO_2, SO_3, Cl, S, NiO, and, in some cases, MnO.

Another, and equally important reason for completeness is

[1] Cf. Washington, Prof. Paper, 99, p. 31.

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that evidence is accumulating, as analyses of a high degree of completeness become more common, that much light may be thrown upon petrological problems of great interest by a knowledge of the presence of the rare elements. The subject has been discussed by Hillebrand,[1] whose strong plea for completeness it will be well for the student to read. An illustration given by Hillebrand may be cited here. The analyses of the U. S. Geological Survey show that baryta and strontia are almost invariably present in the igneous rocks of the United States, and that the former is uniformly in greater amount than the latter. Furthermore it is made clear that, while never present in large amount, they are both more abundant in the rocks of the Rocky Mountain region than in those to the east and west of this. As Hillebrand says: "Surely this concentration of certain chemical elements in certain geographical zones has a significance which future geologists will be able to interpret, if those of to-day are not."

Similarly, we now know, through the complete analyses inaugurated by the chemists of the U. S. Geological Survey, that titanium is not the rare element it was formerly believed to be, but is ninth in order of abundance of the elements that make up the known crust of the earth, being present to the amount of about one-half of one per cent.[2]

Another interesting result of the determination of the rarer elements is the discovery that certain of them are associated more especially with magmas of certain characters, but are seldom found in rocks derived from magmas of other chemical types.[3] Thus, it has been shown by Hillebrand[4] that vanadium is most abundant in rocks that are low in silica, while it is absent, or nearly so in the highly siliceous rocks; conversely molybdenum is confined apparently to the highly siliceous rocks.[4] It is now well-known that high percentages of zirconium and of the rare earths are most frequent in highly sodic rocks, while notable amounts of

[1] W. F. Hillebrand, Jour. Am. Chem. Soc., **16**, p. 90, 1894; Bull. 422, p. 16; H. S. Washington, Prof. Paper, 99, p. 16.

[2] Cf. F. W. Clarke, The Data of Geochemistry. U. S. Geological Survey Bulletin 616, pp. 27, 34, 1916.

[3] For a discussion of this subject and references see Washington, Trans. Am. Inst. Min. Eng., **30**, p. 735, 1908.

[4] Hillebrand, pp. 20, 21, 148.

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chromium or nickel are seldom met with in rocks that are not high in magnesia and iron and low in silica and alkalies.

This leads directly to the consideration of a final point in favor of the present contention, namely, the light that may be thrown on the origin and formation of ores, and the possibility of such chemical study of the igneous and metamorphic rocks leading in the future to important economic advances in the indication of the presence of ore bodies. The researches of Sandberger and others [1] have shown that many of the heavy metals, such as antimony, arsenic, bismuth, cobalt, copper, lead, silver, tin, uranium, and zinc, are present in the pyroxenes, hornblendes, biotites and olivines of some igneous rocks, and can be readily detected if sufficiently large amounts are taken for analysis. Further consideration of this topic is uncalled for here, but, from the point of view of the mining engineer and of geological surveys, it is clear that this is a weighty argument in favor of completeness and the determination of minor constituents in the making of chemical analyses of rocks.

While it follows from the above that all rock analyses should ideally be as complete as it is possible to make them, yet the practical considerations of time and labor may set limitations on this. Although by judicious management a number of the minor constituents can be determined along with the main ones, and at the cost of very little extra time, yet it is true that a thoroughly complete analysis will take considerably longer than a simple one. The analyst must judge for himself how far he can profitably go in this way, but it should be borne in mind that a few complete analyses will probably be of more value in the end than a larger number of incomplete ones.[2]

While it is probable that all or nearly all of the known elements may occasionally be present in rocks, and can be detected if sufficiently large amounts are taken for analysis, in practice we must, for the purposes of this volume, confine our attention to those which may reasonably be looked for in igneous, metamorphic, and many silicate sedimentary rocks, and which may be readily estimated in quantities of from one-half to two grams of material. Those

[1] F. Sandberger, Zeits. Deutsch. Geol. Ges. **32**, p. 350, 1880; Zeits. Prakt. Geol., 1896; cf. J. H. L. Vogt, Zeits. Prakt. Geol., 1898, pp. 225 ff.

[2] See page 16 for a suggestion as to a practical procedure in regard to this.

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which will be considered in this book are given in the following list, which is substantially that of Hillebrand:

$(SiO_2, TiO_2, ZrO_2, Al_2O_3, Fe_2O_3, Cr_2O_3, V_2O_3, B_2O_3, (Ce, Y)_2O_3)$ $(FeO, MnO, NiO, CoO, MgO, CaO, SrO, BaO, CuO)$ (Na_2O, K_2O, Li_2O) H_2O, CO_2, P_2O_5, Cl, F, SO_3, S.

In addition, such elements of rare occurrence in igneous rocks as carbon (as graphite or organic matter), glucinum, lead, molybdenum, nitrogen, tin, or zinc, may be present in determinable amount, but these occurrences are so seldom met with, and the determination of such constituents involves so complicated methods that they will not be considered in this book.

In the great majority of rocks the constituents of the list just given are by no means of equal importance, and it is customary to divide them into " main " and " minor " constituents.

Main Constituents.—Speaking generally, the main constituents are SiO_2, Al_2O_3, Fe_2O_3, FeO, MgO, CaO, Na_2O, K_2O, H_2O.

These nine (including both oxides of iron) are almost invariably present in greater or less amount in all igneous and metamorphic silicate rocks, and positively must be determined in every rock analysis if it is to conform to even the first requirement as to completeness.

The only possible exceptions would be certain rare and little-known types, with which the student is not likely to meet. Thus, in iron ores produced by differentiation of an igneous magma, or in dunites, the amount of alkalies may be so small as to be negligible for most purposes. Or, in the case of very highly quartzose dikes of igneous origin, such as have been described from Africa and Australia, the determination of lime and especially magnesia may be omitted. But even in such rocks it is far better to prove definitely that these constituents are absent or present, even if only in traces. In the light of physico-chemical investigations of extremely dilute solutions, this knowledge may be of great interest and importance in the future.

Stress must be laid on the importance of the separate determination of both oxides of iron, which have been only too often unseparated and reported in the analysis as either Fe_2O_3 or FeO. Neglect of this point was especially common up to thirty years ago, and is the cause of the relative worthlessness of many of the

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older analyses.[1] It is clear that, as the two oxides play different roles in the composition of minerals, a knowledge of the relative amounts of each is necessary to a proper understanding of the rock magma, the calculation of the mode (actual mineral composition) of the rock, or for its classification along chemico-mineralogical lines. Although the error involved by their non-separation may be small in certain highly quartzose or feldspathic rocks, as granites, rhyolites, trachytes and syenites, in which they do not amount together to more than one or two per cent, yet the conscientious analyst should always make it a point to determine them separately.

Water is often present in very notable amount, and should therefore be reported in every rock analysis, even though it is true that the amount of water is not vital to our knowledge of the rock magma, except, of course, when minerals containing water of crystallization or hydroxyl, such as analcite and muscovite, are present; yet its determination is important in that it gives a measure of the freshness of the rock. There is all the more reason for doing this both on account of the ease and celerity of the determination and on account of the fact that its neglect may seriously affect the summation of the analysis. It is also evident that the determination is essential in the investigation of many metamorphic and sedimentary rocks, and in the study of rock weathering and alteration, where hydrous minerals, as chlorite, zeolites, and limonite, are present.

Water may be present as either or both "hygroscopic" and "combined" water, which are expelled from the rock powder at temperatures respectively below and above about 110°, the conventional temperature. There is considerable difference of opinion as to the advisability of the separate determination of these, as well as to the reporting of the hygroscopic water in the analysis. The arguments for and against their separation have been discussed by Hillebrand,[2] and need not be repeated here. While the matter is not of great importance, it may suffice to say that I concur with the opinion of Hillebrand in recommending their separate determination and inclusion in the statement of the analysis, and also in the use of air-dried material for analysis.

[1] Cf. Washington, Prof. Paper, 99, pp. 15, 21, 26.

[2] Hillebrand, pp. 57–63.

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Apart from the constituents discussed above, there are a number of usually minor ones, which may in some rocks assume equal importance with, or even far surpass, some of the main constituents enumerated above. While examples of this are uncommon, yet their number is rapidly growing with increase in our knowledge of the less well-known rocks of the globe, and many of them are of special interest from the theoretical side. As examples there may be cited titaniferous ores produced by differentiation, as those of the Adirondacks, the apatite—rich nelsonites of Virginia, such sodalite- and haüyne-rich rocks, as tawite, taimyrite, and haüynophyres, the eudialyte-rich lujavrites of Kola and Greenland, or the apparently igneous pyritiferous ores of Norway. In these, certain constituents which are usually regarded as minor, TiO_2, P_2O_5, Cl, SO_3, ZrO_2 and S, respectively, are of an importance equal to that of any of the nine mentioned above, and it is clear that an analysis of such rocks which does not take these usually minor constituents into account is seriously defective.

Minor Constituents.—The minor constituents differ much in their relations to the analysis. Those of one group are precipitated and weighed with some of the main constituents (as has been mentioned above), and their weight is afterward to be subtracted from that of the mixed precipitate. Therefore, if they are not determined the apparent amount of the main constituent, which is determined by difference, will be too great. This is true, for instance, with the oxides of titanium, zirconium, chromium, vanadium, and phosphorus, and the rare earths. These are all precipitated and weighed with the alumina, and if any one of them is disregarded it will increase by its weight the apparent amount of the alumina. The resultant error may not be large but, being avoidable, should not be committed by the careful analyst.

Of these minor constituents, the most important are titanium dioxide and phosphorus pentoxide, which are almost invariably present and in most rocks in quantities so large as to cause serious error in the figure for alumina if their determination is neglected. These two should, on this account, be determined in every rock analysis, or its value may be notably diminished, because knowledge of the exact amount of alumina is a very important factor in chemico-mineralogical rock classifications, as well as in the calculation of the mineral composition. The others are seldom present

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in amount greater than a few tenths of one per cent and usually much less, so that neglect of them will not often involve appreciable error in the figure for alumina. Zirconia is apt to occur in notable, though small, amounts in rocks that are high in soda, so that it is well to determine zirconia in such rocks, while chromium sesquioxide and vanadium pentoxide [1] may be determined in rocks that are high in magnesia and iron and low in silica.

Analogous cases are strontia, lithia, and manganous oxide. The first of these is precipitated and weighed with lime, being afterward separated from this to arrive at the true weight of the lime. Similarly, lithia is weighed with soda, thus increasing its apparent amount. But both strontia and lithia (especially the latter) are present in such minute amounts that their non-determination will seldom affect the figures for lime or soda to an appreciable extent. They are chiefly of interest from the theoretical side, and this applies more especially to strontia.

The case of manganous oxide is more complex, and for its discussion we must anticipate some features of the analysis. If the alumina is precipitated with ammonia water, as is usually done some of the manganese comes down with the alumina, a little of it comes down later with the lime, and the rest falls with the magnesia.[2] It is clear, therefore, that unless the manganous oxide is completely separated from the alumina, and if it is not precipitated before the determination of lime and magnesia, it will be distributed among these three constituents.

On the other hand, whi e it may be completely separated from the alumina by what is known as the " basic acetate " precipitation, and then precipitated as sulphide before lime and magnesia are determined, yet this procedure is liable, as we shall see pp. (149, 155), to cause serious errors in the determination of alumina and iron oxide; likewise it is tedious and involves about one day's extra time.

Fortunately manganous oxide is present in very few rocks in greater amounts than two or three-tenths of one per cent, so that

[1] Vanadium pentoxide is also later precipitated and weighed with the phosphorus pentoxide, so that its amount should be subtracted from that of the latter, not from that of the alumina. See page 216.

[2] This distribution of manganese has been studied by G. Steiger, in the U. S. Geological Survey Laboratory. Cf. Hillebrand, p. 114; Mellor, p. 371.

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even if it is neglected and its weight distributed among alumina, lime, and magnesia, the error will not usually be serious, and may be regarded as negligible.

Manganous oxide can, however, be thrown down with the alumina by ammonium persulphate, so that it will not subsequently affect the figures for lime and magnesia. It can be determined separately by a colorimetric method, and its weight can then be subtracted from that of alumina. This is the best procedure in the great majority of rock analyses, and we can say that manganous oxide should always be determined colorimetrically, although it need not be separated from the other more important constituents if its amount is very small.

The second group of minor constituents consists of those whose determination or non-determination does not affect the figures for any of the main constituents. This includes nickel, cobalt, copper, and barium oxides, sulphur, sulphur trioxide, chlorine, fluorine, and carbon dioxide.

Of these the first three occur as a rule only in traces in igneous rocks, nickel more abundantly in the less siliceous ones; in these it may be well to determine it. Indeed, the determination of nickel is advisable in very particular analyses of intermediate to basic rocks, and is always necessary in analyzing meteorites, though neglect of it will seldom if ever lead to serious error in dealing with terrestrial rocks. Copper cannot be considered an important constituent, but it may well be looked for in rocks low in silica, as it may be of theoretical interest.

As has been mentioned above, barium is a constant constituent of the igneous rocks of the United States, and it is almost certain that it will be found to be widely distributed elsewhere when it is looked for systematically. In view of its theoretical interest and the comparative ease of its determination by the method given beyond, it will usually be advisable to look for it in the course of the analysis.

Sulphur is very frequently present as the sulphides pyrite and pyrrhotite, and indeed much more often than was formerly believed, especially in the less siliceous rocks. Its amount can be readily ascertained along with the baryta and it should enter into the statement of most analyses, or its absence be definitely shown.

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Sulphur trioxide and chlorine are met with in igneous rocks with comparative frequency, especially in rocks that are high in soda, and both are always to be determined if minerals of the sodalite group are present. It is always well to determine them in rocks liable to carry such minerals, even if these are not visible with the microscope. In other rocks also it can scarcely be held to be a great loss of time to look for them, in view of their possible theoretical interest and the ease of their determination.

Fluorine is seldom present in quantities over a few tenths of a per cent and need not often be looked for. This may be done, however, if the rock contains fluorine-bearing minerals, but even here its determination is necessary only if these are abundant or for very accurate work.

Carbon dioxide is often present in igneous and metamorphic silicate rocks, but, as far as is now known with certainty, only when the rock is not strictly fresh, as a component of the secondary minerals, calcite, dolomite, siderite and cancrinite. If it is present it should always be determined, because it serves to a certain extent as a measure of the freshness of the rock, and because the result may have a bearing on the problem of its occurrence as a primary constituent.

It is to be remembered that if water is determined as "loss on ignition," this will include the carbon dioxide, which is also expelled. The latter must, therefore, be determined separately and directly.

As a final and practical solution of the difficulty in deciding what constituents to determine the following procedure is suggested.[1] If only one or two rocks are to be analyzed, especially if they come from a little-known locality, the analysis should be as complete as time and other considerations will permit. But if a series of analyses is to be made of the rocks of a region or volcano that includes various types, two analyses should be made of each of the most important or most abundant types, and but one analysis of a representative of each of the less important. All of these analyses should show the amounts of the main constituents, as well as the minor ones, TiO_2, P_2O_5, and MnO, including the usually minor ones which may be of major importance. The rarer constituents, such as ZrO_2, Cr_2O_3, BaO, SrO, and NiO, need only be

[1] Cf. Washington, Prof. Paper, 99, p. 17.

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determined in one each of the more important types. This may be regarded as the optimum compromise between the ideal and the practical.

5. The Occurrence of Various Elements

The increased number of analyses of igneous rocks, especially of those of unusual types, and the more frequent determination of the minor constituents, with the mass of data obtained by the use of the microscope, have shown that certain of the rarer elements are prone to occur in rocks of certain chemical characters. While our knowledge along this line is far from complete, a few words may be devoted to this subject, as it will often be of use to the analyst to know which elements should be especially looked for and which may safely be neglected.[1] The various minerals which carry the several elements in question will also be mentioned as well as the amounts in which the elements usually occur.

Titanium is invariably present, as shown by all rock analyses in which it has been sought for, and it is ninth in order of abundance among the elements making up the crust of the earth. Its amount is very small in the more quartzose and feldspathic rocks but it is most abundant in the more femic rocks. It is an essential component of ilmenite and perofskite, which are most common in femic rocks, and of titanite, which occurs in rocks with more silica. The oxide rutile is rare in igneous rocks, but is common in metamorphic ones. Titanium also enters into some magnetite and hematite, and also very commonly, but to a less extent, into pyroxenes, amphiboles, biotites, garnets and other ferromagnesian minerals. Its amount in rocks may vary from less than, and seldom over, one per cent, to five or more per cent reckoned as TiO_2.

Zirconium is present in many rocks in small amount, and is apt to occur in granites, pegmatites, rhyolites, syenites, and in nephelite syenites, phonolites, and tinguaites. It is most

[1] See also F. W. Clarke, Bull. U. S. Geol. Surv., 78, pp. 34–42, 1891; J. H. L. Vogt, Zeits. Prakt. Geol., 1898, pp. 225 ff.; F. W. Clarke, Bull. U. S. Geol. Surv., 168, pp. 13–16, 1900; Bull. U. S. Geol. Surv., 616, pp. 13, 39, 1916. J. F. Kemp, Ore Deposits of the United States, New York, 1900, p. 35; Hillebrand, Bull. 422, p. 23; H. S. Washington, Trans. Am. Inst. Min. Eng., 30, p. 809, 1908; J. P. Iddings, Igneous Rocks, 1, 1909, p. 27.

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abundant in rocks which are high in soda, such as the last three. It is rarely met with in rocks, rich in lime, magnesia, and iron. Zirconium is usually found as the silicate zircon, especially in granites and syenites, but is also an ingredient of such rare minerals as eudialyte, låvenite, and rosenbuschite. Zirconium is present usually in amounts less than 0.20 per cent of ZrO_2, but may rarely reach 2 per cent or more.

The *rare earths*, oxides of cerium and yttrium, and of their congeners, are found, so far as known in notable amount only in rocks that are high in soda. They form part of allanite, a mineral that is rather widespread in granites, and also of monazite, mosandrite, xenotime, and other minerals of even greater rarity. They are almost always accompanied by notable amounts of zirconia. The rare earths, reckoned as $(Ce, Y)_2O_3$, seldom are present in more than one-tenth of one per cent, but two rocks are known in which they are present to the extent of about 0.4 and 0.6 per cent. Scandium has been shown to be widespread in traces.

Chromium is almost wholly confined to the femic rocks, especially those which are high in magnesia and low in silica, and which consequently contain abundant olivine, such as peridotite and dunite. It occurs as chromite and picotite (chrome-spinel), and in a few augites, biotites and olivines. It may occur up to one-half of one per cent of Cr_2O_3.

Vanadium, according to the investigations of Hillebrand, "predominates in the less siliceous igneous rocks and is absent, or nearly so, in those high in silica." It is an ingredient of pyroxenes, hornblendes, and biotites, but not of olivine, and is also present in the ilmenite of some titaniferous iron ores. Its amount is always very small, seldom over 0.05 per cent of V_2O_3.

Manganese is uniformly present in nearly all rocks, but its amount is small, generally in tenths of a per cent as MnO, being only very exceptionally one-half of one per cent or more. The high figures commonly reported are, in most cases, regarded as due to analytical error, an opinion in which Dr. Hillebrand concurs. It occurs in the ferromagnesian minerals, pyroxenes, amphiboles, micas, olivines and garnets, and therefore is usually present in greatest amount in the more femic rocks. It seems to favor rocks high in iron rather than those high in magnesia.

Nickel and cobalt, like chromium, are most abundant in olivine

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rocks, but the former has been noted in certain basalts. They occur as ingredients of olivine, as well as in pyrite and pyrrhotite, and in hornblende and biotite to a small extent. The amount of nickel in terrestrial rocks is seldom more than 0.05 or 0.10 per cent, while that of cobalt is only exceptionally more than a trace. In some analyses nickel has been undoubtedly reported too high, probably having been confounded with contaminating platinum.

Copper is often to be found in igneous rocks, but as a rule merely in traces. It is probable that the copper reported in some analyses of igneous rocks is really platinum derived from the platinum basin and crucibles, while again it may be due to contamination from the copper water baths, etc. It is most frequent in the more femic rocks, such as diabase, gabbro, and basalt, entering the pyroxene and amphibole, as well as being a component of chalcopyrite, and in traces in some pyrite. It also (rarely) occurs as the metal.

Barium and strontium are very commonly present in igneous rocks, the latter uniformly in less amount than the former. There is some evidence that barium is apt to be most abundant in rocks which are high in potash. Barium occurs in the feldspars, especially orthoclase, as the celsian molecule, in the rare hyalophane, in some zeolites, as well as in a few biotites and muscovites. We can, at present, form no definite conclusion as to the character of the rocks most likely to carry strontium, and more analytical data on this point would be of interest. The amount of BaO may reach 1 per cent, though it is usually much less, while that of SrO may run up to 0.30 per cent, but, as a rule, is little more than a trace.

Lithium is an element of very widespread occurrence, but is seldom met with in rocks in more than spectroscopic traces. It may be expected to be most abundant in highly alkalic rocks, and there is reason for the belief that it is especially prone to occur in sodic ones. Apart from its occurrence as an essential constituent of such minerals as lepidolite and spodumene, which occur in highly silicic pegmatites and granites, it is also found in the alkali feldspars, muscovite, beryl, and other minerals.

Phosphorus is almost invariably present in igneous and metamorphic rocks, like titanium, and like this element it is most abundant in the more femic ones, especially in those which are high in lime and iron rather than in magnesia. It occurs almost

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solely in apatite, or very exceptionally as xenotime or monazite. While the quantity of P_2O_5 usually runs from 0.10 to 1.50 per cent, generally under 1 per cent, it may occasionally amount to much more.

Sulphur, as sulphides, is far more abundant in the femic rocks of all kinds than in the salic ones, and forms an essential ingredient of pyrite and pyrrhotite, and the rare mineral lazurite. As sulphur trioxide (SO_3) it occurs in the minerals haüynite, noselite, and lazurite, and usually in the more femic rocks, though some haüynite rocks carrying quartz are known. These three minerals are most apt to occur in rocks which are high in soda. Sulphur, as sulphides, is present usually in tenths of a per cent, as is also true of SO_3, though in certain cases the amount may be much higher. It is a common error to report sulphur as SO_3 instead of as S.

Chlorine is present most abundantly in rocks which are high in soda, and especially when so low in silica that nephelite is present, though it is also found sometimes in nephelite-free rocks, and in a few cases in quartz-bearing ones. It is an essential component of sodalite and noselite, and is also present in scapolite and in a few apatites. It also occurs, as sodium chloride, in liquid inclusions. The amount of Cl is usually a few tenths of a per cent, but in sodalite rocks it may be 1 per cent or more.

In specimens of rocks collected near the sea coast the presence of chlorine may be due to contamination by sea water. This should be ascertained and determined by leaching the rock powder.

Fluorine as a component of apatite, biotite, etc., seems to have no special preference as to magma, though, on the whole, it is found more frequently in silicic than in femic rocks. It is, however, most apt to be met with as fluorite and some other rare fluorine-bearing minerals, in rocks that contain nephelite, as foyaites and tinguaites. It is an essential constituent of fluorite and most apatite, and as an integral part of the last mineral is almost universally present. It also occurs in small amount in biotites and other micas, in some hornblende and augite, as well as in tourmaline, topaz, chondrodite, etc. Its usual amount is very small, generally from traces to 0.10 per cent, only rarely being above the latter figure.

Of the other rare elements it may be of interest to note the

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following. Glucinum, as a component of beryl and some other very rare minerals, is most frequent in granites, pegmatites and quartzose gneisses; it seems to be most at home in sodic rocks. There is reason to think that the high alumina sometimes reported for these rocks may be in part glucina, which has not been separated from the alumina, and due to the presence of unidentified beryl. This is a point worthy of investigation, but, so far as I am aware, glucinum has never been looked for or determined in an igneous rock. Tin, as the oxide cassiterite, is confined to the highly silicic rocks, granites and pegmatites, and its presence is due generally to pneumatolytic processes. It also may occur in traces in ilmenite, micas, and feldspars. Thorium would seem to be most abundant in highly sodic rocks, and the same is also apparently true of radium and the radioactive elements.[1] Molybdenum, tungsten, and uranium are almost exclusively confined to the very siliceous rocks. Zinc has been met with in granite, as well as in basic rocks, but no generalization in regard to it is possible as yet. Platinum is found almost exclusively in peridotites, but is occasionally met with in connection with gabbros. Boron, usually as a constituent of tourmaline, is most apt to occur in highly siliceous rocks.

6. Statement of Analyses

The results of the analysis might be stated in terms either of the elements present or of the basic oxides and acid radicals.[2] While the former may be the more logical on purely theoretical grounds, yet the latter greatly facilitates calculations based on the analytical data, and being universally in use, renders comparison of all rock analyses with each other very simple. It should therefore be adopted without question.

The order in which the constituents are tabulated varies somewhat widely though now much less so than formerly. In some cases the order is roughly that in which the constituents are determined in the course of the analysis. Elsewhere one finds the acid radicals placed first, followed by the basic oxides. Or SiO_2 is followed immediately by Al_2O_3, or sometimes first by TiO_2,

[1] Cf. A. Holmes, Geol. Mag., (6), 2, p. 63, 1915.
[2] Cf. Mellor, p. 251; Ostwald, pp. 212–215.

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and then by the more important basic oxides, generally including MnO, with the less abundant constituents following these.

There is general unanimity only in heading the list with SiO_2. In regard to all the other substances reported there has been very considerable diversity in the details of sequence. Thus CaO sometimes precedes and sometimes follows MgO, and the same is true of Na_2O and K_2O. This lack of uniformity is to be deplored, as it is not only extremely apt to lead to error in copying analyses the order of statement of which is unfamiliar, but it also renders needlessly difficult the comparison of two or more analyses tabulated according to different systems.

Some years ago it was proposed [1] that petrographers and chemists follow a definite and uniform plan in the statement of the analyses of rocks, and the order then suggested with the reasons for its adoption are briefly given here. It may only be added that no cogent reason has been brought forward for any important modification, and that it has been adopted in its essentials by the chemists of the U. S. Geological Survey.[2]

The general foundation for the order proposed is that analyses of rocks are intended primarily for the benefit of petrographers and petrologists, so that an arrangement along analytical or strictly chemical lines is neither advantageous nor appropriate. To them the eight oxides, SiO_2, Al_2O_3, Fe_2O_3, FeO, MgO, CaO, Na_2O and K_2O, which are present in preponderating amount, in the vast majority of rocks are, and must always remain, of prime importance. H_2O and CO_2, which are also often present to a very notable extent, are of value as measures of the freshness of the rock. The other constituents, while of varying interest, are usually present in small or minute quantities, and influence the character of the rock only to a limited extent. The order suggested, with a few slight modifications, is:

SiO_2, Al_2O_3, Fe_2O_3, FeO, MgO, CaO, Na_2O, K_2O, H_2O+ ($>110°$), H_2O- ($<110°$), CO_2, TiO_2, ZrO_2, P_2O_5, B_2O_3, SO_3, Cl, F, S(FeS_2), (Ce, Y)$_2O_3$, Cr_2O_3, V_2O_3, MnO, NiO, CoO, CuO, (ZnO), BaO, SrO, Li_2O.

By putting the eight main oxides together and at the head,

[1] H. S. Washington, Am. J. Sci., **10**, p. 59, 1900.

[2] The only noteworthy difference is that in the practice of the Survey the positions of H_2O+ and H_2O- are interchanged.

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the general character of the rock may be seen at a glance. Furthermore, whether an analysis is complete or incomplete, these oxides are always in the same relative position, and, as they are (or should be) determined in every case, the eye finds them without trouble, thus greatly facilitating comparison and study.

As regards the main portion, we start out with the chief acid radical and the constituent which is present in largest amount, and pass through successively lower orders of oxides to the most positive bases, the alkalies. At the same time they are presented in a way which brings the oxides together in their natural petrographic and mineralogic relations. Alumina, which often apparently has an acidic function and which is usually the most abundant constituent next to silica, follows immediately after this, and is succeeded by the other main sesquioxide, ferric oxide. Ferrous oxide follows ferric, and magnesia is next to it, as the two go hand in hand in the ferromagnesian minerals. Lime comes next in an intermediate position between these and the alkalies, as is proper, because it is a constituent both of the ferromagnesian minerals and of the feldspars. Soda precedes potash, as it is associated with lime in the plagioclases.

Water follows immediately after the main oxides, since it is an important and a generally determined constituent. Combined water precedes hygroscopic, being the more important and almost invariably present in greater amount than the latter. Carbon dioxide comes next, as it, with water, is a measure of the freshness of the rock, and this character can therefore be told at a glance. They also constitute together the "loss on ignition" so frequently given, and may then be connected by a bracket in comparative tabulations.

Of the minor constituents the acid radicals come first, their sequence following the main principle of the other division. Titanium and zirconium dioxides are placed at the head, as they are chemically similar to silica, and often replace it. Phosphorus pentoxide comes next as it is usually, next to titanium dioxide, the most important and abundant of the minor constituents. Boric oxide is very seldom determined but, in case it is looked for, its proper place would be just after phosphorus pentoxide. Sulphur trioxide and chlorine are together, since both of these are constituents of the sodalite group of minerals. Fluorine follows

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immediately after chlorine, both being halogens. Sulphur completes the list of the minor acid radicals, being less acidic than the others; it is also frequently present as a constituent of apparently secondary origin and is thus analogous to water and carbon dioxide among the main constituents.

The subordinate metallic oxides follow in the order R_2O_3, RO, and R_2O. Among the sesquioxides those of the rare earths (though they are seldom determined), come first, as they appear to be isomorphous with alumina mineralogically. Chromium sesquioxide precedes vanadium as it is the more important. These two might be placed among the minor acid radicals, but the position chosen seems the best. Manganous oxide precedes the oxides of nickel and cobalt, as it is very frequently determined, and is present in greater amount. The monoxides of the other heavy metals when present come next, those just mentioned preceding on account of their greater importance and their chemical affinity with ferrous oxide. Of the oxides of the minor alkali-earth metals, which are next in order, baryta precedes strontia as the more abundant and important. Lithia closes the list as the only minor representative of the alkali metals.

In publishing the analysis it may be recommended that the molecular numbers of each of the constituents, (obtained by dividing the percentage amount by the molecular weight), be given along with the regular statement. The user of the analysis will thus be saved the trouble of calculating them for himself, and the chemical character of the rock will be more fully and immediately comprehended.

In the statement of analyses the term " trace " is in frequent use, to indicate that a constituent is present, or supposed to be present, in a small but undetermined amount. The use of the term has been loose, and in some rocks quite erroneous, as more complete analyses have shown that such " traces " may amount in reality to one-half of one, or possibly to several per cent. It would be better to have the meaning of the term more strictly defined, and it has been suggested[1] that it " should indicate strictly and uniformly that the constituent (to which it is applied) has been looked for and found, but in unweighable amount (0.1 milligram or less)." If there is no knowledge as to the presence

[1] H. S. Washington, Prof. Paper 99, p. 16.

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of a substance a dash may be used. Hillebrand suggests that, "In the tabulation of analyses a special note should be made in case of intentional or accidental neglect to look for substances which it is known are likely to be present." For this purpose the letters "n. d." (not determined) may be reserved. The absence of any constituent, if looked for, should always be stated in the tabulation and not in the accompanying text, as is sometimes done, since the fact is thus apt to be overlooked.

The analytical calculations should be carried to four decimals, which means that in the statement of analyses the figures are to be given to hundredths of a per cent. While the last decimal may not be of much significance, it represents the limit of weighing (0.0001 gram) in the quantities taken for the determination of the constituents of rocks, and gives some assurance of the value of the preceding decimal. It is also the almost universal practice among chemists and analysts.[1] Statement in only tenths of a per cent is defective in that it implies correctness only in the unit column, and consequently an insufficient degree of accuracy. It is also of an inadequate degree of accuracy for the minor constituents.

On the other hand, a statement in thousandths of a per cent implies a higher degree of accuracy than is possible with the limits of error obtaining in all but the most painstaking analytical work, and which is quite uncalled for in view of the somewhat variable composition of all rock masses from place to place, however great may be the apparent uniformity. It may be remarked that, in the course of compiling and examining thousands of rock analyses, I have found it to be true, almost without exception, that the few analyses given to thousandths of a per cent are remarkable chiefly for their poor quality, differing from the probable truth in some or all constituents by as much as one or more per cent. Statement in such ultra-refined terms may usually be regarded as evidence that the analyst has no just appreciation of the probable limits of error, or of the bases of accuracy in analytical work.

A final word must be said in regard to the recalculation of

[1] This topic is well discussed by Mellor (p. 16), who says: "As a matter of fact, two decimals are generally used in technical analyses because we have grown accustomed to the plan, not because it represents the accuracy of the work." Cf. Washington, Prof. Paper, 99, p. 22.

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the analysis to an even 100 per cent.[1] This is tantamount to the distribution of any errors over all the constituents, which is not justifiable, as has been said elsewhere. Furthermore, as Fresenius says, " such ' doctoring ' of the analysis deprives other chemists of the power of judging of its accuracy." Whatever the results may be, and whether the summation be high or low, the figures for the various constituents should be given with their summation, as they are obtained from the analysis, if the whole is deemed to be worthy of publication at all. Any other procedure would give rise to reasonable suspicion as to the accuracy of the analysis, which can only be judged of by others if the actual figures are given.

[1] Cf. Mellor, p. 246.

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PART II

APPARATUS AND REAGENTS

ALTHOUGH any well-equipped laboratory should have nearly every piece of apparatus and all the reagents which are necessary for the quantitative analysis of rocks, it may be convenient, especially for the independent worker, to give a list of those that should be available, and which will be needed, during the progress of a properly carried out analysis. Brief remarks will be made on certain points which it is useful for the inexperienced to know. The number of pieces of apparatus suggested are those which it is deemed advisable to have at hand, so that a series of analyses may proceed without interruption for lack of adequate facilities; and the amounts of reagents suggested are such as it will be well to provide when stocking up an individual laboratory.

Suggestions as to general laboratory equipment are not made, as this is usually provided for the student and can seldom be radically changed. It may be well, however, to emphasize the importance of a hood with a good draught, provision of a steam-bath, an efficient arrangement for suction, and, above all, proper arrangements for keeping the laboratory clean and free from dust and fumes.

1. APPARATUS [1]

BALANCE AND WEIGHTS [2]

Balance.—A good, reliable, and accurate balance and weights are essential to good analytical work. It cannot be impressed

[1] In connection with many of the pieces of apparatus references are made to the figures in the catalogues of Eimer & Amend, New York, 1913 edition (E. & A.), and of Arthur H. Thomas Company, Philadelphia, edition of 1914 (A. T. Co.), so that the correct form can be identified.

[2] Cf. Fresenius, 1, p. 12; Gooch, p. 11; Mellor, p. 3; Morse, p. 1; Treadwell, 2, p. 6; P. J. Krayer, The Use and Care of a Balance. Easton, Pa., 1913.

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too strongly on the beginner that the value of his analytical work rests fundamentally on the quality of his balance and weights and on the care with which they are treated. The other apparatus may be adequate, the reagents of the utmost purity, the methods of the best, and the manipulation careful, delicate, and conscientious; but if the balance and weights are not accurate, and are not carefully taken care of, the labor and time expended on the analysis will largely or wholly go for naught. The balance and weights should, therefore, be regarded with a feeling akin to reverence, and the balance-case be looked upon, so to speak, as a sanctum sanctorum.

There are several good balances, of moderate cost, on the market that will answer all the requirements for any but the most exacting work. Only a high-grade, analytical (not a so-called "student's") balance, of a reliable maker, should be selected.

The capacity should be 200 grams, with a sensibility of one-tenth of a milligram at full load. The bearings should be of agate, the beam of magnalium or some such light and not easily corrodible metal, and graduated for a rider.

As summarized by Mellor, the conditions which must be satisfied by a good balance are: 1, it must be consistent, that is, give the same result in successive weighings of the same body; 2, it must be accurate; 3, it must be stable, so that the beam after being displaced will return to its horizontal position; 4, it must be sensitive; 5, in order to avoid loss of time in weighing, the beam must oscillate quickly, and must therefore be short.

It will be convenient to adjust the sliding or screw weight on the pointer or beam so that one (small) division of the scale will correspond to 0.1 milligram. It is important that the zero point be determined from time to time. For most work it is not necessary to determine it before each weighing, as is recommended by some, but it should be borne in mind that some balances are liable to change of zero point with change of temperature.

The balance must be, of course, in a case, with appropriate releases for the knives and pans. The case is always to be kept closed when not in use. A 2-inch funnel, filled with granular calcium chloride, and supported in a small Erlenmeyer flask, is to be kept in the back part of the case. Sulphuric acid should never be used as a desiccating agent in a balance. The case and

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pans are to be kept free from dust by light brushing with a camel's-hair brush from time to time.

In reading the pointer it is convenient to use a "balance reading glass" mounted in front of the ivory scale. For setting the beam to swinging a very useful adjunct is a rubber hand-bulb, connected with a tube passing through the floor of the case, and permitting a puff of air to be blown against the bottom of one of the pans.[1] The balance should also be provided with a small, light metal stand for holding tubes, as well as a shelf to straddle the pan for specific gravity determinations.

The location of the balance is a matter of importance. It is discussed by Morse, and we can hardly do better than summarize what he says. The essential points are:

1. The balance case should be in a room separate from the laboratory, where it is free from corroding gases.

2. It should be so located that the two arms will maintain, as nearly as possible, the same temperature and consequently the same length. Hence it should not be placed near a window, especially one with southern exposure, or a source of heat, such as a radiator, stove, or hot air vent. It must not be placed where it will be in direct (or even reflected) sunlight at any time of the day or year.

3. The source of light, especially if artificial, should be above and back of the head of the observer, and so located with respect to the beam that the heat from it will affect both arms equally. Diffuse daylight from a window at one side, if somewhat in the rear of the observer and not very near, will answer.

4. The foundation upon which the balance sets should be as firm as possible, and any jarring or vibration from machinery is to be avoided. A heavy table with stout legs (which may be made of iron piping), and with a stone slab for a top answers well. The top must be strictly horizontal. There should be sufficient space on it for the note-book and desiccator.

For cautions as to the use of the balance, see the section on weighing, pp. 79, 129.

Weights.—The weights should be of the "first quality" of

[1] So far as I know this is provided only with the Rüprecht balances. It should be better known and more widely used, as it is, by far, the best device for its purpose.

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the catalogues. The set should run from at least 50, or better 100, grams down to 1 centigram. The weights below the 10 milligram weight are not needed, as the rider is always used instead of them. The gram weights are best made of brass, preferably gold or platinum plated, though Krayer advocates the use of first-quality lacquered brass weights. The smaller weights are of platinum. The weights may be kept in their box (covered) in front of the case, though some prefer to keep them, arranged in order, in the balance case in front of the right-hand pan.

The weights should never be touched with the fingers, but are always to be handled with the ivory-tipped forceps that should accompany them. The handling with these should be most gentle, and there must be no rubbing or scraping of the neck of the larger weights in putting them back in their places. They must be kept free from the action of any dust or corroding vapors, and must never come in contact with any solid or liquid chemicals. If kept in the box, this is always to be closed after use. The weights are to be occasionally lightly wiped (not rubbed) with a silk handkerchief.

For accurate work the weights should be tested. The description of this process is rather too long, and the student is referred to Gooch (p. 21), Mellor (p. 16), Morse (p. 26), or Treadwell (p. 15).

It is assumed that the laboratory has a cheaper and less accurate balance, capable of weighing up to 1 kilogram or so, and set of weights, to weigh out reagents roughly and in large amounts.

Platinum [1]

A number of utensils of platinum or of a substitute for it are indispensable for analytical work. The present price of platinum is so high that for many chemists, unless they are the fortunate possessors of an old stock, a substitute must be used. Fortunately, this is to be found in the recently introduced alloy (80 gold, 20 palladium), called "palau." According to the investigations of the Bureau of Standards, this compares very favorably with platinum, and practically all the usual analytical operations that are carried out at temperatures not much above

[1] For a report by Hillebrand, Walker, and Allen on the quality of recent platinum see Jour. Ind. Eng. Chem., 3, p. 686, 1911.

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1250° C. (approximately that of an ordinary blast) can be done equally well in palau. The only exception would be, apparently, the fusion with pyrosulphate, which attacks palau somewhat more than it does platinum. Palau, however, suffers less loss of weight by vaporization than platinum.[1] In the following list, therefore, and throughout this book, when platinum is mentioned it will be understood that palau may be substituted for it, with the possible exception of the crucible for the pyrosulphate fusion (p. 159).

List of Apparatus.—One basin, lipped, of about 300 c.c. capacity, 10 to 11 cm. across the top, and about 5 cm. deep, weight about 100 grams. This should not be hemispherical, but with a somewhat flatly rounded bottom and vertical upper sides (E. & A., 5340, A. T. Co., 44116). If the edge is stiffened with wire this should not be continued around the lip or, if so, the turned edge should be soldered with platinum (or palau) around this, to prevent entrance of liquid and possible contamination or loss. Instead of a platinum basin one of chemically pure gold (free from copper) will serve, and good porcelain may be used in work that is not very accurate, though it is difficult to remove all silica from this. Neither fused silica nor glass should be used for the main evaporation to determine silica.

Four crucibles; two of about 35 c.c. capacity, and two of about 25 c.c. Each should have its own cover, with which it is always weighed. For the main fusion with sodium carbonate the crucible, if of platinum, should be of metal alloyed with rhodium or iridium to give stiffness (p. 132). The slight loss of weight due to volatilization is of no moment here, as the weight of the crucible after the fusion is not taken. Palau is sufficiently stiff to do well for this fusion. One of the 25 c.c. crucibles, for the pyrosulphate fusion, would best be of pure platinum.

One Gooch crucible, $3\frac{1}{2}$–4 cm. high, 3–$3\frac{1}{2}$ cm. wide at the top, and $2\frac{1}{4}$–$2\frac{1}{2}$ at the bottom, of about 25 c.c. capacity, it should have a cover. A close-fitting cap for the bottom of this is a convenience. A porcelain Gooch may be used instead (p. 99).

One small, shallow-lipped basin, of about 50 c.c. capacity, and weighing about 20 grams.

One spatula, in one piece, about 10 cm. long and weighing about

[1] For a study of the quality of platinum see Burgess, Scient. Papers, Bur. Stand., Nos. 254 (1915) and 280 (1916).

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10 grams. It should be rather thick, with round, broad end, and no handle.

Two triangles, one of 5 and one of 6 cm. along the side. The style with twisted ends is good, if the ends are smooth it is well to make a series of small notches along one end to support a crucible cover (p. 104).

As some platinum crucibles may adhere to platinum triangles, triangles of clay or fused silica have advantages other than those of low cost, and are indeed recommended. Those made of silica tubing strung on nickel or nichrome wire answer well in place of platinum. If one has both platinum and palau crucibles and triangles the different metals must never be in contact when hot.

One perforated, seamless cone, about 2.5 cm. in diameter.

One pair of crucible tongs, platinum tipped, of brass or German silver, and of the usual shape. One of Blair's form, with platinum or palau shoes, will also be useful.

A pair of blowpipe forceps, with platinum or palau tips, is necessary if blowpiping is to be done, and is very useful in separating mineral grains for analysis.

A few small pieces of platinum foil, cut into strips and bent at right angles or in zigzags, are used to prevent boiling liquids from "bumping" (p. 165).

Care of Platinum.—All or nearly all platinum and palau crucibles lose weight [1] (palau less than platinum), when heated above about 900°, especially on blasting (about 1200°). With platinum the loss is apparently due in part to the iridium content. The rate of loss for each crucible used should be ascertained; or, if serious, the empty and cleaned (not scrubbed with sand) crucible should be weighed after an ignition.

There are several precautions to be observed in the use and care of platinum [2] (and palau) utensils.

Platinum utensils must be kept bright and clean; this applies especially to crucibles. It is best accomplished by rubbing the crucible with sea sand moistened with water. The grains must be rounded and the sand free from grit. I have found sand from

[1] Cf. Hillebrand, Bull. 422, p. 94, footnote; Burgess and Sales, Jour. Ind. Eng. Chem., **6**, p. 452, 1914; 7, p. 561, 1916; Sci. Pap. Bur. Stand., No. 254, 1915; Burgess and Walters, Sci. Pap. Bur. Stand., No. 280, 1916.

[2] Cf. Mellor, p. 115.

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the New Jersey coast excellent. The whole lot of sand should be well washed, digested with warm, dilute hydrochloric acid for some time, to remove fragments of shells, and then washed again and dried. The crucible should not be deformed in the rubbing. A crucible should be sand-rubbed quite frequently, especially after a long ignition, as it prevents and removes surface crystallization and coating, and greatly prolongs the life of the crucible.

If the sand rubbing does not remove firmly adherent particles of ignited precipitate or stains, these may be removed by fusing a little potassium pyrosulphate in the crucible. If the stain is on the exterior the salt is fused in a larger crucible or in a small basin in which the crucible that is to be treated is immersed. Because the pyrosulphate attacks the metal this cleansing should be done as seldom as possible and the fusion is not to be continued longer than necessary.

Hot platinum must never be touched with any other metal. Therefore it should only be handled with the platinum-tipped tongs, and should not rest on red-hot wire gauze, whether of iron or nichrome. In heating the platinum basin over a Bunsen burner it is well to have the center of the gauze asbestos covered. No metals or salts of heavy or easily reducible metals should be heated or melted in it.

Sulphides, arsenides, and phosphides should not be heated in platinum, and in the ignition of phosphates care should be taken that no reduction takes place.

Fused alkali carbonates attack platinum very slightly (p. 146), but fused caustic alkalies, as well as fused alkali nitrates and baryta, attack it seriously. Platinum is also very appreciably attacked by fused potassium pyrosulphate, so that the crucible shows a very decided loss of weight after each fusion with this salt.

As platinum is readily attacked by free chlorine, platinum must never be exposed to this. Consequently, it should never come in contact with a mixture of hydrochloric acid and a strong oxidizing agent which would give rise to free chlorine. If manganates are present, they should be reduced, as by alcohol, before the addition of hydrochloric acid.

Platinum should not be exposed to burning carbon, as coke or coal, though the flameless burning off of the carbonized filter paper does no damage. It should not be heated in a smoky or luminous

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flame, nor in the inner cone of the Bunsen burner. The air supply of this must be so adjusted that the flame is non-luminous.

Platinum should not be exposed to violent changes of temperature, such as exposure when red-hot to a blast of cold air or immersion in water, and the crucible must not be bent or squeezed as is frequently recommended, to loosen a fused cake. A little care and patience will obviate the need of such measures, and the loss of a little time is preferable to the misfortune of a dented and distorted, and possibly cracked and ruined, crucible.

GLASS

At the present time the formerly much-used Jena and Kavalier glasses are almost unobtainable, and will probably continue so for years to come. This, however, is of no consequence, as there are now produced in the United States [1] several makes of chemical glassware that are equal to, and in some respects excel, the best of the German glasses, such as Pyrex, Nonsol, Insol, Fry and others. The Pyrex is especially valuable because of its very low coefficient of expansion, which permits thicker walls and consequently less liability to breakage, either mechanically or by sudden changes of temperature. Official tests [2] have shown that such glasses are entirely satisfactory in all essential respects, such as resistance to solutions of acids, alkalies, and various salts, and to hot and cold water, and sudden changes of temperature, proper annealing, correct shape, and uniformity. All beakers and flasks used in the analysis should be of such resistant glass.

Beakers should be on hand in liberal quantity. They should all be lipped and of the usual form; the low (Griffin's) and the tall forms are seldom if ever needed. It is convenient, but not necessary, to have a small space ground or etched on the side for writing on. The following number of each size would best be kept at hand: Three 1000 c.c., four 800 c.c., five 600 c.c., six 400 c.c., six 250 c.c., five 200 c.c., ten 150 c.c., ten 100 c.c., five 50 c.c.

Burettes.—It is best to have two types of these. There should be two Ripper's [3] weight-burettes (E. & A., 1354), one of 50 and

[1] I understand that similar glass is now made in England.

[2] See Walker and Smither, Jour. Ind. Eng. Chem., 9, p. 1050, 1917.

[3] M. Ripper, Chem. Zeit., p. 793, 1892.

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one of 100 c.c., for the iron determinations. These should have glass caps to cover the tips, and a wire loop to support them on the hook above the balance pan.

Some of the advantages of a weight-burette over one of the usual form are:[1] Correction for temperature changes is not needed, adherence of liquid to the walls is of no consequence, the solution can be weighed readily to 0.01 gram, whereas measurement to 0.01 c.c. is very uncertain.

If the burettes become stained brown by manganese, the stain can be readily removed with a little solution of sulphur dioxide. The burette is to be very thoroughly washed out after its use.

There should be also two burettes of the ordinary, Mohr's type (E. & A., 1314, A. T. Co., 22,556), with glass stopcock, preferably set at an angle of 90°. These are of 50 c.c., graduated to tenths of a cubic centimeter, and should preferably be "certified." Such devices as Erdmann's float, meniscus reader, and enamelled strip on the back are not needed.

Carbon Filter Tube.—(E. & A., 3228, A. T. Co., 28,036). One should be selected of a size to fit the Gooch crucible that is in use, with allowance for the rubber connection. The tube is to be provided with a singly perforated rubber stopper to fit the filtering flask. A rubber filtering gasket (A. T. Co., 27,749) or crucible holder may be used instead with an ordinary funnel.

Desiccators.—One desiccator, either of the Fresenius (E. & A., 2546, A. T. Co., 25,870) or the Scheibler (E. & A., 2528, A. T. Co., 25,830) type, with a pipe stem triangle, serves for general use. Granulated soda-lime or calcium chloride should be used as the drying agent, as sulphuric acid may give off sulphur dioxide by the action of dust. It is convenient to have also a larger, Scheibler, desiccator, containing a porcelain plate with several holes, in which crucibles, etc., can be put aside. A desiccator with a stopcock for drying in vacuo is sometimes useful, but is not necessary for general work.

Drying Cylinders.—A good type is that with perforated glass stopper and side tube near the top (E. & A., 7128, A. T. Co., 23,200). Two or three, of medium sizes, will do.

[1] R. S. McBride, Bull. Bur. Stand., **8**, p. 617, 1912; see also E. W. Washburn, Jour. Am. Chem. Soc., **30**, p. 40, 1908.

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Drying Tubes.—These are best of the U shape, and preferably of the Schwartz type. Three or four, of medium sizes, will serve.

Flasks, both of the ordinary, flat-bottomed and Erlenmeyer shapes, may be of the following sizes: Ordinary, flat-bottom; two each of 400, 200, 100, and 50 c.c.; Erlenmeyer, three each of 500, 300, and 200 c.c.

Flask, Filtering.—This should be of the Erlenmeyer shape, thick-walled, and with a side tube (E. & A., 3090, A. T. Co., 28,248). The capacity should be 500 c.c.

Funnels.—There should be two of 75 mm., three of 65 mm., and two of 50 mm. in diameter. Care should be taken to select these with an apical angle of exactly 60° and perfectly straight sides.

The ground-off point is to be cut off, and a tube about 22 cm. long, and internal bore of 3 mm., bent into a circle of 2 to 2½ cm. near the upper end, is fused to the stem of each. It is important that the junction be smooth and without enlargement. This tube greatly promotes rapidity of filtration, by the suction of the column of liquid, the formation of which is established by the liquid collecting in the bend.[1] The narrow tube must not be attached to the stem by a bit of rubber tubing, because of the liability to loss or contamination of the filtrate through creeping of liquid between the rubber and glass.

A small funnel, 4 cm. in diameter and with straight stem about 7 cm. long, is needed for small filtrations; and another 5 or 6 cm. in diameter, with the stem cut off half-way, slightly drawn out, and bent at about 120°, is used for introducing the hydrochloric acid into the platinum basin (p. 137). It is well to have on hand several other ordinary funnels, of various sizes.

Gas Generators.—Kipp's form (E. & A., 2674, A. T. Co., 29,572) is about the best. There should be one each, of medium size, for carbon dioxide and hydrogen sulphide.

Gas Washing Cylinders.—A good type is Muencke's (E. & A., 1044, A. T. Co., 29,472), and another about equally good is Drexel's tall form (E. & A., 1036, A. T. Co., 29,452). There should be two or three of medium sizes.

[1] See Ostwald, p. 14. It is somewhat surprising that such funnels, which have been in common use for many years, are not listed in the dealers' catalogues.

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Glass Cells (E. & A., 6334), with parallel sides, for colorimetric determinations (p. 43). A pair with identical internal distance between parallel sides will be needed.

Measuring Cylinders.—These should be lipped and not stoppered. They should be reasonably accurate, but it is not necessary that they be "certified." There should be one each of 10, 25, 100, and 500 c.c.

Measuring Flasks.—These should all be stoppered, and it is best to purchase them "certified," as these will need no calibration for ordinary, good work. One each of 1000 and 500 c.c., and three each of 250, 200, and 100 c.c. will suffice.

Pipettes.—Two each, of 5 and 10 cc. and one of 50 c.c., with the bulb in the middle of the stem, are sufficient. Their capacity should be indicated by marks above and below the bulb.

Separatory Funnel.—One pear-shaped, separatory funnel, with glass stopcock and stopper, and rather wide stem, may be needed occasionally for mineral separations with heavy solutions. A capacity of 100 c.c. is about the right size.

Specimen Tubes.—There should be a supply of several dozen of these, with round bottoms, and with smooth corks to fit. Appropriate sizes are: $4\times\frac{1}{2}$, $4\times\frac{3}{4}$, and $5\times\frac{5}{8}$ inches, of which the first will be the most generally used.

Stirring Rods.—The diameter of these should not be over 3 mm.; it is common with beginners to use too thick stirring rods. About twenty should be prepared, of various lengths, from 10 to 22 cm. long; the shorter stirrers being made of the thinner rod. Both ends should be rounded, and about 2 cm. of one end bent back sharply at about 60°. It is not well to use stirring rods that are alike at both ends, because of the danger of mistaking the immersed part (with adherent solution or precipitate) for the clean end.

One of the long and one of the medium stirrers should be provided with a rubber "policeman." The narrow shape (E. & A., 6032, A. T. Co., 46,164) is about the best for general use. An exellent one may be made [1] from a No. 00 (10 mm.) solid rubber stopper, by boring a small hole half way through axially from the small end, removing the core, and cutting and grinding down the larger end to a smooth wedge.

[1] Suggested by Dr. J. C. Hostetter.

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Test Tubes.—A few each of different sizes, from small to medium (say 10×1.2 to 16×2 cm.) should be kept.

Thermometer.—A thermometer, reading to 150° at least, and preferably to 250°, is needed for the hot-air oven. This may have an opal glass scale. It will also be well to have one or two more, with scale etched on the stem, one reading to 300°, for various purposes.

Tubing.—One will need sufficient tubing of rather soft glass and of various diameters for making connections, etc. There should also be a supply of special glass tubing, of an internal diameter of 5 or 6 mm., for the determination of water. This tubing may be either thick-walled and of soft glass, or (better) thin-walled and of refractory glass, but not as refractory as combustion tubing. The glass must not devitrify on heating, as often happens with old glass.

Wash-bottles.—Two main wash-bottles are needed. These should be of resistance glass, flat-bottomed, and of 1000 c.c. capacity. The tip, with an exit hole 1 mm. in diameter, is attached by a short length of rubber tubing. About 5 cm. of the lower end of the exit tube should be bent at about 120°, so that the intake is near the lower side wall, and in the same plane and direction as the tip. This enables more of the liquid to be expelled than if the tube is straight. One of these wash-bottles, for hot water, has its neck protected against the heat. This may be done with asbestos paper, which is wrapped around in several thicknesses and moistened, when it adheres; or with a thin sheet of cork, bent entirely round the neck and held in place by copper wire. The latter is preferable, as the asbestos paper is liable to flake off and contaminate the material in the process of analysis.

There should also be a wash-bottle (500 c.c.) reserved for the dilute ammonia water used in washing the magnesia precipitate, and another (300 c.c.) reserved for the alcohol used in the alkali determination. It is best to have these with glass stoppers (E. & A., 1132, A. T. Co., 48,960) as ammonia and alcohol attack rubber, and it is well to label each specially. A spare, 300 c.c. wash-bottle will be convenient for various washing solutions.

Watch-glasses.—Six each of 2, 2½, 3, 3½, 4, and 5 inches, and three each of 6, 6½, and 7 inches, should be on hand. It will be convenient to have one each of the 4-, 5-, and 6-inch glasses per-

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forated with a central hole about 5 mm. in diameter. A watch-glass is always to be placed on a beaker with the convex side down.

A pair of the 2½- or, better the 3-inch glasses, weighing very nearly alike, should be adjusted to equal weight by filing the edge of the heavier. These are used in weighing out fluxes, and are to be marked with a diamond and kept in the balance case.

FUSED SILICA

Because of its high melting-point, resistance to all acids (except hydrofluoric), constancy in weight under ignition, and low coefficient of expansion, fused silica, which can now be obtained of very good quality and in a great variety of forms, may replace platinum for some purposes. In selecting utensils made of it, care must be taken to see that the interior surface is "flashed," that is, rendered quite smooth by intense heating, so that no bubble cavities are open to the interior surface. If the interior surface is thus made smooth it is not necessary that the material be of the more expensive, transparent variety. Strongly alkaline liquids should not be heated for long in fused silica vessels.

Basin.—This must be lipped. One about 13 cm. in diameter and 7 cm. deep, with a capacity of about 500 c.c., will serve for the alkali determination.

Beaker.—It is well, but not necessary, to have a fused silica beaker for the alkali determination. This is best of 400 c.c. capacity, and lipped.

Triangles.—Instead of platinum or palau triangles, those made of fused silica may be used with advantage, as they are much cheaper and there is no liability of the crucible sticking to the triangle. Those made of tubing strung on nickel or nichrome wire are excellent.

PORCELAIN

There are several very good makes of American, as well as Japanese and Copenhagen, porcelain on the market, which are quite equal to, and very satisfactory substitutes for, Royal Berlin and other German makes. The porcelain should be glazed inside and out.

Casseroles.—These should be lipped and with porcelain han-

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dles. Covers are not needed. One or two each of 165 and 135 mm., with possibly a smaller one, will be enough.

Crucibles.—Two or three of different sizes, with covers, are useful. One about 5 cm. in diameter may be reserved as a "radiator" for the evaporation of sulphuric acid in platinum crucibles, but a nickel crucible is better (p. 145). A porcelain Gooch crucible, 35 or 40 mm. in diameter, may replace one of platinum. It is well to have with this a circular, perforated disc of porcelain.

Evaporating Dishes.—Two or three each of 9-, 10-, 12- and 15-cm. lipped, should be on hand.

Plate.—A square, white, porcelain plate, 12 or 15 cm. in diameter, is useful for titrations, as well as for the separation of minerals.

RUBBER

Funnel.—A hard rubber funnel, of the smallest size, is needed for filtration of liquids containing hydrofluoric acid, if one of platinum is not available.

Stoppers.—There should be a selection of several sizes, perforated with one and two holes.

Tubing.—A variety of different sizes, for making connections, should be available. There should also be about 1 foot of black, soft, thin-walled tubing for Gooch crucibles (E. & A., 6064, A. T. Co., 46,236), of a diameter appropriate to the crucible in use.

METAL

Burners.—Three or four Bunsen burners should be provided. The Tirrill type (E. & A., 1462, A. T. Co., 22,884) is very convenient, as it permits easy adjustment of both gas and air. One Meker burner (E. & A., 1468, A. T. Co., 22,916), of medium size, is useful for ignitions at higher temperatures.

There should also be available a blast Bunsen burner of the usual type.

Clamps.—There should be on hand several clamps of different types and sizes. A large-sized one of the "universal" type (E. & A., 2034, A. T. Co., 24,508), with rubber-covered jaws, is used to hold the weighing burette. There should be also several clamp fasteners.

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Hot Plate.—An electric hot plate with three "heats" is very useful.

Igniter.—An igniter, made of cerium-iron alloy, which can be obtained at any hardware store, is useful and preferable to matches.

Mortar.—A hardened steel mortar is necessary for the crushing of the rock specimen. It is imperative that the steel be as hard as possible, to avoid contamination by iron. The mortar should also be readily taken apart and freed from all the rock powder, and easily cleaned. It should also be sufficiently large to take in a rock fragment 2 or 3 cm. in greatest dimension.

The best known to me is the type devised and made by C. W. H. Ellis, mechanician in the Geophysical Laboratory of the Carnegie Institution of Washington. These are made of a "special tool" steel, hardened by Mr. Ellis, by a treatment of his own.[1] They are made in different sizes. One of the largest, used in the U. S. Geological Survey laboratory, is figured by Hillebrand,[2] with its dimensions given.

These mortars are of the Plattner style, in three pieces, base, cylinder, and pestle, but the cylinder is very high, to guard against loss of fragments and dust. They are all larger than the Plattner "diamond" mortars ordinarily obtainable. The pestle may be of two forms; one with a large knob at the upper end (as figured by Hillebrand), for use with the hand alone, the pestle acting as hammer; and the other slightly tapering toward the top, for use with a hammer. The base may be square or round. The bottom of the cavity in the base is flat, the cylinder fitting snugly into the cavity, while the pestle has a little play in the cylinder. The dimensions of the one I use, which is of the knobless form, are as follows: Base, 6 cm. square, 2.5 cm. thick; cavity, 3.2 cm. diameter, 0.5 cm. deep; cylinder, 8 cm. high, 3.2 (scant) external and 2.6 internal diameter; pestle, 11.5 cm. long, 2.5 cm. diameter at base, 2.4 at top.

If one of these is not procurable, a first-quality, three-piece, "diamond," Plattner's mortar may be used. It is important that the steel be as hard as possible, a point to which especial attention should be paid, that the pestle fit somewhat loosely in

[1] The hardness of mine is 8.

[2] Hillebrand, Bull. 422, p. 51.

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the cylinder, and that the bottom of the cavity be flat.[1] Those usually listed in the dealers' catalogues (E. & A., 4626, A. T. Co., 40,808) are intended for blowpiping, and are too small for convenient use with rock specimens, though they will serve.

The steel mortar should be exposed as little as possible to the fume-laden atmosphere of the laboratory, and ought to be kept in a tightly closed box, to prevent rusting. It should not be handled with moist fingers, and after use should always be immediately wiped dry with a clean and dry cloth and placed in its box. It should never be "left around" exposed to the air and, of course, must not be greased or oiled, however lightly.

Nickel Crucible.—A nickel crucible, used as a radiator, is better than one of porcelain for the evaporation of sulphuric acid (p. 145), as the operation is more quickly carried out. One 5 cm. in diameter, 4 cm. high, and of about 60 c.c. capacity, is of convenient size.

Oven.—A copper oven with single walls is needed. A convenient size is 8×6×6 inches. One shelf is sufficient. It should be provided with legs or a suitable tripod support.

Retort Stands.—At least three, and preferably four, should be on hand. The base should be rectangular—not triangular, as these are very unstable. The rod may be 16 or 18 inches high. Rings, with clamp attached, 3 inches in diameter are most useful, but it is well to have also a 4-inch ring. It is well to have one of the 3-inch rings with three interior knobs (A. T. Co., 46,072) for supporting the porcelain crucible in evaporating sulphuric acid. It is unwise to have more than one ring on the stand at a time. The rod may advantageously be covered with a piece of glass tubing closed at the top, to prevent the falling of rust. The retort stands and rings should be wiped off frequently. There is constant danger of contamination by iron rust from them, and it would be well if some made of nickel, nichrome, or some such non-rusting metal were on the market.

Water Baths.—If the laboratory is not provided with a steam bath, two water baths should be on hand. These are to be of

[1] The recommendation of a hemispherical cavity (first edition, p. 51), applied only to the two-piece, Leed's form. It was corrected in the second edition, p. 54.

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copper, preferably with porcelain rings, and fitted with a Kekulé regulator. (E. & A., 628, A. T. Co., 49,048.)

Wire Gauze.—Two squares each, of 4 and 5 inches, are needed. These are best made of nichrome wire, as they do not rust and long outlive those of iron. It is well to have one with an asbestos-covered center for heating the platinum basin.

MISCELLANEOUS

Agate Mortar.—An agate mortar, about 9 cm. in outside diameter, is needed for the preparation of the rock specimen. One should be selected that has no soft spots or rough streaks, at least in the interior. The pestle should be embedded firmly [1] in a wooden handle with cement and a brass collar, making the whole about 2½ inches long. It will be useful, but not necessary, to have another larger agate mortar, about 13 cm. in diameter. The pestle of this needs no handle. Substances should only be ground, never pounded, in an agate mortar.

Burette Stand.—One for two burettes is needed. A very convenient type is the Chaddock (E. & A., 6548, A. T. Co., 22,692) with rubber-covered wire spring clamps and white glass base.

Colorimeter.—A colorimeter is needed for the colorimetric determination of titanium dioxide, manganous oxide, and chromic oxide. The simple form described by Hillebrand [2] is very satisfactory and serves all ordinary purposes. The more elaborate forms devised by Schreiner (E. & A., 2116, A. T. Co., 24,738) and Steiger [3] are excellent but much more complex and expensive.

The essential part of the simple form, whose use is assumed in the operations described later, is a pair of glasses or glass cells, of square or rectangular section. Two opposite sides of each must be parallel, and the interior distances apart of these sides in the two glasses must be identical, at most within 1 per cent of the distance. The other sides need not, but would best be, parallel, and may be blackened to exclude light. The glasses used by me are 12 cm. high, and 4 cm. between the parallel sides each way.

These glasses are made of thin (2–3 mm.) plate glass, cut to

[1] Mine has been in use for over twenty years and is still firm.
[2] Hillebrand, p. 33; Mellor, p. 84.
[3] Hillebrand, pp. 37, 35.

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size, and cemented with a cement that will resist the action of dilute acids. The angles may be strengthened by rubber tape.

The use of a suitable box is necessary to exclude side lights, and that illustrated by Hillebrand serves well. This may be made easily from a box in which are packed the ceresine bottles containing one-half pound of ammonia water or hydrofluoric acid.

The box measures $20 \times 9.5 \times 9.5$ cm. internally. The square bottom is removed, leaving the box open at either end. A 3-inch square of ground glass is substituted for the sliding cover, the glass slipping snugly into the grooves, which may need a little widening with a penknife. About 5 cm. of the side next to the free edge of the glass is then cut away, to allow the insertion of the pair of glasses. This side now becomes the top of the box. A thin wooden partition (made of the cover of the box) is inserted through a narrow slot cut clear across the top of the box alongside the glasses away from the ground glass. This shutter should slide stiffly up and down, so as to remain at any desired height, or a thin wedge may be used to hold it in place. The box and partition are blackened inside and out, and the result is a box that is light and compact enough to be held easily in the hand.

Filter Papers.—Round-cut filters are to be used, the paper being of such quality as to leave but a negligible amount of ash, filter fairly rapidly, and yet retain the finest precipitates. They must be "double-washed" with hydrochloric and hydrofluoric acids, of the type of the Schleicher and Schüll No. 590. Baker and Adamson, "A" quality, is excellent, and some of the Whatman paper will serve. The sizes in regular use are: $5\frac{1}{2}$-, 7-, 9-, and 11-cm., of which there should be two packages each and one of $12\frac{1}{2}$ cm. The filters are to be kept in a drawer away from dust.

Funnel Supports. Two wooden funnel supports should be sufficient. My preference is for the single-arm type for two funnels, with one hole larger than the other. The two-arm type takes up (often) unnecessary space, and the two arms cannot be differently adjusted as to height.

Horn Spoon.—One about 12 cm. long is used for weighing out fluxes. It may conveniently be kept in the balance case.

Labels.—A box of medium small labels, such as Dennison's No. 217, should be on hand.

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Sieve.—A sieve [1] for preparing the rock powder is made of a cylindrical glass box, about 8 cm. diameter and 4½ cm. high. Closely fitting this is a brass ring, about 1 cm. wide, which holds in place a 4-inch square of silk bolting cloth. To prevent the loss of dust (p. 69) the brass ring may be 2 cm. wide and a second glass box of the same diameter as the first fitting into the upper half of the ring, acts as a receptacle for the rock powder.

Silk Bolting Cloth.—That which is best for preparing the sample is of 100 mesh (40 meshes to the centimeter). Three square feet of this had best be kept. Some of 50-mesh will be useful for mixing the sample (p. 71).

Stone Slab.—A useful adjunct is a small slab of some igneous rock, such as granite, on which to cool crucibles. This may be 4×3×1 inches, and is polished on the top face. A steel block of about the same size may be used, but should be nickel- or gold-plated to prevent rusting.

Support.—A Gay-Lussac or Schellbach "universal," wooden support will often be found useful.

Test-tube Rack.—One of wood for six tubes, with draining pegs, should be sufficient.

2. Reagents

The matter of the quality of reagents [2] is most important, and one that is far too often neglected. Only those of the very best quality should be used, and these cannot always be taken on faith. It is a good precaution to test even the so-called "guaranteed" or "analyzed" reagents for impurities, by the methods suggested by Krauch,[3] Merck,[4] and Fresenius [5] and in some cases for impurities not considered by them. This is because, while they are generally satisfactory, yet mistakes will occur and it is very difficult to free some reagents from certain impurities. As Hillebrand says:

[1] Sieves such as these are useful for many separations and they might well be listed in the dealers' catalogues.

[2] Cf. Fresenius, 1, p. 49; Hillebrand, Bull. 422, p. 39; Mellor, p. 141.

[3] C. Krauch, Trans. by Williamson and Dupré, The Testing of Chemical Reagents for Purity. 1902.

[4] E. Merck, Trans. by H. Schenck, Chemical Reagents, their Purity and Tests. 1914.

[5] Fresenius, Qual. Anal., pp. 52 ff., Quant. Anal., 1, pp. 127 ff.

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"A C. P. label is no guarantee of the purity of a reagent," and samples of "guaranteed" reagents have been found to be worse than some without any special guarantee.[1]

In recent years there has been a great improvement, and the "guaranteed reagents" furnished by such makers as Baker and Adamson, The J. T. Baker Chemical Co., and Squibb are generally excellent.

It is well to stock up with amounts of reagents (except the strong acids and ammonia water), sufficient to last for a very considerable time, and to test each new lot once for all. It must be said, however, that the "guaranteed" concentrated hydrochloric, nitric, and sulphuric acids, and hydrofluoric acid (in ceresine bottles), are nearly always reliable and scarcely need special testing, except that nitric acid is to be examined for chlorine.

All the reagents in use, on the work-bench shelves, are to be kept in glass-stoppered bottles[2] of good quality; the narrow-mouth ones (best with a vertical flat stopper) are kept covered with loose-fitting glass caps, and the wide-mouth ones should have a flat stopper projecting over the lip, to keep off dust. It is best, when possible, to have the labels either etched or ground on the glass (E. & A., 958, 976, A. T. Co., 22,270, 22,304), or, better, enamelled (E. & A., 950, A. T. Co., 22 328). Paper labels should be varnished. The strength of standard solutions should be written on the label.

It may be convenient to give a list of the different sizes of reagent bottles appropriate for the reagents in most general use. Most of these can, and all ought to be obtainable (of the dealers) in these sizes with permanent labels as mentioned above.

Narrow-mouth Bottles, 500 c.c.—Alcohol, ammonium hydroxide,[3] ammonium molybdate, ammonium nitrate, hydrochloric acid, nitric acid, potassium chromate, standard manganese solution, silver nitrate, standard titanium solution, sulphuric acid (conc.), sulphuric acid (1 : 1).

[1] In this laboratory "guaranteed" ammonia water has been found to contain zinc; potassium chromate, crystals of potassium nitrate; ammonium acetate, much cadmium; and magnesia, about 3 per cent of lime.

[2] Cf. Mellor, p. 142.

[3] The bottle should be coated internally with ceresine or paraffine, or a ceresine bottle is used in place of glass. See p. 48.

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250 c.c.—Acetic acid, barium chloride, chloroplatinic acid, ether, hydrogen peroxide, magnesia mixture, potassium thiocyanate.

Wide-mouth bottles, 500 c.c.—Ammonium carbonate, ammonium chloride, ammonium oxalate, calcium carbonate, ferrous sulphide, sodium ammonium phosphate, sodium carbonate, potassium pyrosulphate.

250 c.c.—Ammonium nitrate, ammonium persulphate, asbestos, sodium acetate, potassium nitrate.

In the following list of reagents (with the exceptions of alcohol, ammonia water, hydrochloric, hydrofluoric, nitric, and sulphuric acids), amounts are suggested that should be sufficient to last several years, in ordinary analytical work. They should all be " guaranteed reagents " with the exception of a few that are noted.

Acid, Acetic (250 grams).—Acid of 30 per cent strength will answer for use in the sodium acetate method.

Acid, Hydrochloric [1] (6 pounds).

Acid, Hydrofluoric (2–8-ounce bottles).—This must be obtained and kept in ceresine bottles (never in rubber or gutta percha). The greatest possible caution should be observed in its use, as a sore produced by it may last for years.

Acid, Nitric (7 pounds).

Acid, Sulphuric (9 pounds).

Alcohol, Ethyl, Absolute (8 ounces).—This is only used in the determination of strontium. The stopper should be very close-fitting.

Alcohol, Ethyl, "95 Per Cent" (2 quarts).—This should be of good quality, not denatured, and it is well to filter it. For use in the determination of alkalies it is diluted with distilled water to a specific gravity of 0.86. If a hydrometer is not available, this specific gravity may be attained approximately by mixing five volumes of alcohol with one of water. The liquids are to be measured out separately, because of the contraction that takes place on mixing.

Ammonium Carbonate (1 pound).—This should contain no non-volatile matter and only a trace of tarry matter. The solution is made as needed.

[1] Commercial hydrochloric acid will serve for generating carbon dioxide and hydrogen sulphide. The strength should be 1 : 1.

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Ammonium Chloride (1 pound).—This is not likely to contain impurities that render it unfit for the alkali determination, for which alone it is used, but it should be tested to see that it contains no non-volatile matter. Re-sublimation is seldom called for. It should not be used for the addition of ammonium chloride in the main portion of the analysis, where it is formed instead by the neutralization of hydrochloric acid by ammonia.

Ammonium Hydroxide (4 pounds).—This must leave no solid residue on standing or on evaporation, and it must be free from carbonate. Immediately before use a small portion should be tested with calcium or barium chloride. If ammonium carbonate is present the ammonia water is to be boiled to decompose the carbonate.

Ammonia water (" guaranteed ") may be purchased in ceresine bottles, but its delivery in this material is not a guaranty that it has not been kept in glass. It is best to make it from time to time by passing ammonia gas from a cylinder through (previously boiled and cooled) distilled water contained in a ceresine bottle. This should be only half full and surrounded with water and cracked ice. The gas should be passed until the specific gravity is 0.92. The purity of the reagent thus prepared will compensate for the trouble involved.

Ammonia water, intended for analytical work, should never be kept in glass, as this is inevitably attacked more or less, rendering the reagent impure. For the best work, indeed, glass vessels should not be used for precipitations, etc., in ammoniacal liquids.[1]

The reagent is best kept in ceresine bottles, with a tight-fitting ceresine stopper that is closed by a screw motion, and covered with a loose-fitting glass cap. It may be kept in a glass bottle coated all over the interior with ceresine, by putting a few pieces into the perfectly dry bottle, gently warming the bottle, and spreading the wax by turning the bottle around. This coating, however, is likely to loosen in time and allow the ammonia to attack the glass, so that a ceresine bottle is preferable.

Ammonium Molybdate (1 pound).—This salt is usually sufficiently pure for use without testing. The solution used in the determination of phosphorus pentoxide is prepared by dissolving 50 grams of ammonium molybdate in 250 c.c. of water, with the

[1] Cf. Allen and Johnston, Jour. Ind. Chem. Eng., 2, p. 202, 1910.

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aid of heat, and pouring it when cold into 250 c.c. of concentrated nitric acid, with constant stirring. The precipitate that first forms redissolves on addition of all the ammonium molybdate. The mixture is filtered through an asbestos plug in a funnel, after standing a few days.

Ammonium Nitrate (8 ounces).—A solution containing 340 grams of this to the liter is needed in the determination of phosphorus pentoxide, and the salt is occasionally used in the solid form.

Ammonium Oxalate (1 pound).—It is well to recrystallize this, after filtering, to insure its freedom from calcium oxalate. The solution is made as needed.

Ammonium Persulphate (8 ounces).—The ordinarily pure salt will answer for the colorimetric determination of manganese, but for the precipitation of manganese with alumina the "guaranteed" salt should be specially tested, or purified by the method recommended by Hillebrand.[1] The salt is used in the solid form.

Asbestos (4 ounces).—This should be the "true" asbestos, that is, the amphibole variety, not the chrysotile or serpentine variety, which also goes under the name of asbestos.[2] The former is practically anhydrous and insoluble in acids, while the latter is partially soluble in acids and contains about 13 per cent of water, which is lost on ignition, resulting in the breaking down of the fibrous texture.

A good quality, perfectly white, silky, but not necessarily very long fiber, should be selected. About 10 or 20 grams is macerated with water in a porcelain mortar, or if of long fiber is scraped down with a knife and macerated with water. The mass is placed in a 400 c.c. beaker, 200 c.c. of water and 20 c.c. of hydrochloric acid are added; the mixture is boiled for half an hour, and allowed to stand over night on the steam bath. It is then well washed with distilled water, and preferably allowed again to stand over night with dilute acid to remove all the soluble iron. Finally it is thoroughly washed with hot water on a large filter (best with suction)

[1] Hillebrand, Bull. 422, p. 102.

[2] Cf. Dana, System of Mineralogy, pp. 389, 670, 1892; F. Cirkel, Chrysotile-Asbestos, Ottawa, 1910, p. 18. Cirkel (p. 282), under laboratory uses does not mention Gooch crucibles.

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to free it from chlorine, and kept, mixed with enough water to form a thin cream, in a wide-mouth, glass-stoppered bottle. There should be no coarse bits of fiber in the final product.

Barium Chloride (4 ounces).—A solution of 20 grams in 200 c.c. of water is used.

Boric Acid (4 ounces).—This may be used in the titration for ferrous oxide (p. 186). It is kept in the solid form.

Calcium Carbonate (1 pound).—This is in powder form, not too fine and light. Only the very best quality should be used, and the amount of alkali (reckoned as NaCl) in 10 grams properly sampled should be determined by the Smith method (p. 193), so as to be able to apply the proper correction. This must never be neglected when dealing with a new lot. If the carbonate is of really good quality, containing less than half a milligram of NaCl in 4 grams, the correction need not be applied, except in very accurate work. The amount of alkali in poor material can be much reduced by long washing with hot water.

Calcium Chloride (1 pound).—This should be in granular form, for use in drying apparatus, and the ordinary " pure " quality will serve.

Chloroplatinic Acid (20 grams).—As it is usually obtained this contains about 37 per cent of platinum. It is used as a solution containing either 0.05 or 0.10 gram of platinum per cubic centimeter. My preference is for the former. To make this, 10 grams are dissolved in 50 c.c. of water in the cold, filtered through a very small filter, the filter washed two or three times, and the filtrate made up to 75 cc. in the reagent bottle. The bottle and cap should be wiped clean frequently. For the calculation of the proper amount to use in the analysis see p. 203.

Chromium Standard Solution.—This is prepared by dissolving 0.1276 gram of pure, normal potassium chromate (K_2CrO_4) in water and making up to 500 c.c.

Dimethylglyoxime (1 ounce).—A little of this is dissolved in alcohol as needed for the determination of nickel.

Ether, Ethyl (8 ounces).—This should be anhydrous.

Hydrogen Peroxide (8 ounces).—Any good brand, such as " dioxogen," containing at least 3 per cent of H_2O_2, will serve. It is scarcely necessary now to test for fluorine, which can be done by the method suggested by Hillebrand (Bull. 422, p. 40). This is

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the only likely impurity that will affect its use in the analysis. As the reagent decomposes on standing, especially if in a warm place or in warm weather, the bottle should not be too closely stoppered, and it is best to purchase it fresh, in small quantities from time to time.

Iron Sulphide (2 pounds).—The ordinary fused, granular or stick form, is used for generating hydrogen sulphide.

Litmus Paper.—A little of both the blue and red will be useful. It may be obtained in small book form or in strips in vials, and is best kept in a wide-mouth, glass-stoppered bottle, painted black or kept in the dark.

Macerated Paper.—This is used in the final precipitation with ammonia water (p. 154), and some is best made up beforehand, as follows: Two or three 11 cm. ashless filter papers are torn in pieces, placed in a small beaker, and moistened with just enough concentrated hydrochloric acid to wet them. After standing for two minutes (not more), distilled water is gradually added, the mass is vigorously stirred, whereupon the paper disintegrates rapidly. The product is freed from the acid by washing under suction and kept, mixed with enough water to make a cream, in a small, wide-mouth bottle. It should be properly labelled so as to distinguish it from asbestos.

Magnesia Mixture.—This may be made by dissolving 10 grams of magnesium chloride and 30 grams of ammonium chloride in 130 c.c. of water and adding 70 c.c. of ammonia water; or by dissolving 20 grams of magnesium sulphate and 40 grams of ammonium chloride in 160 c.c. of water and adding 80 c.c. of ammonia water. In either case the solution is allowed to stand for some days and is then filtered.

Manganese Standard Solution.—This should contain 2 milligrams of MnO in 10 c.c. It is prepared by dissolving 0.2228 gram of the purest, dry, potassium permanganate in 250 c.c. of water. After standing for a day or two, 10 c.c. of sulphuric acid are added, and the permanganate is reduced by the very cautious addition of a solution of sulphur dioxide in water, until the solution just becomes colorless. When cool, it is to be diluted to exactly 500 c.c. in a measuring flask.

Marble (5 pounds).—Any good grade of white marble, not dolomitic, in lumps, will serve to generate carbon dioxide. As

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some marble contains sulphides, the gas must be washed with a solution of copper sulphate, as well as with water.

Methyl Orange (1 gram.)—The solution is made by dissolving 20 mgr. of the dye in 100 c.c. of water. It is most conveniently kept in a small dropping bottle.

Perchloric Acid (4 ounces).—This reagent may be needed for the separation of potash from soda (p. 207). It may be purchased, but is best prepared by Kreider's method, which is described by Treadwell.[1] This consists in fusing sodium chlorate until it is changed into sodium perchlorate and chloride. The melt is dissolved in water, hydrochloric acid is added, and the mixture is evaporated to dryness. The dry mass is treated with an excess of concentrated hydrochloric acid, the solution of perchloric and hydrochloric acids is filtered off from the sodium chloride, and the filtrate evaporated down until the hydrochloric acid is driven off and white fumes of perchloric acid are evolved. Purification from potash is sometimes needed. For details the student should consult Treadwell. Alcoholic solutions of perchloric acid must not be evaporated over a naked flame, for fear of dangerous explosions; evaporation on the steam bath is apparently safe, and evaporation of aqueous solutions is not dangerous.

Potassium Nitrate (1 ounce).—This is occasionally needed for oxidizing sulphides. It is used in a solid form.

Potassium Permanganate (1 ounce).—A solution of a concentration appropriate for use in rock analysis is made by dissolving 1 gram (best weighed to 1 mm.) of the pure, dry salt in 1 liter of water.[2] The solution should stand for one week, to completely oxidize any organic matter in the water, and is filtered through previously ignited asbestos (placed as a loose plug in a rather large funnel) into the stock bottle, before standardization. One c.c. of this solution will correspond to about 0.0025 Fe_2O_3 or 0.00225 FeO.

The standardization may be effected with any of the well-known reagents, such as metallic iron, sodium thio-sulphate, oxalic acid, and ammonium, potassium, or sodium oxalate. The

[1] Treadwell, p. 51.

[2] For descriptions of the preparation and different methods of standardization of the solution, see Treadwell, pp. 90, 597; Mellor, p. 193; Morse, p. 459.

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last is the one recommended.[1] Sodium oxalate ($Na_2C_2O_4$) is readily obtainable pure and dry.[2] It is best to dry it for two hours at 130° in the oven. My procedure, which is essentially that of McBride and Blum, except as to temperature, is as follows: Three portions of the sodium oxalate, of about 0.066 gram each, are weighed out to a tenth of a milligram, dissolved in water and placed in three 400 c.c. beakers. To each is added 5 c.c. of 1 : 1 sulphuric acid, and the volume is brought to about 250 c.c. They are then titrated successively (from a weight burette), at room temperature[3] with the permanganate solution, the liquid in the beaker being stirred vigorously and continuously during the titration. The decolorization takes place very slowly at first, more slowly than with ferrous oxide, and one must wait for this before the addition of another portion of permanganate. The permanganate is to be added in portions, at first, of not more than 1 c.c., and is "not to be added more rapidly than 10–15 c.c. per minute, and the last ½–1 c.c. must be added dropwise with particular care to allow each drop to be fully decolorized before the next is introduced." The end-point is reached when the first pink blush is obtained that does not disappear with a minute's vigorous stirring. For all but the most accurate work, the estimation of "the excess of permanganate used to cause an end-point color by matching the color in another beaker containing the same bulk of acid and water," is an unnecessary refinement. The depth of color decided on as the end-point may vary slightly with different individuals, but that used in the standardization must be adhered to in the iron determinations.

The mean of the three determinations, which should not vary more than 0.1 gram, is taken, and will be, for the amounts taken above, about 30 grams of permanganate solution. As equal

[1] Cf. Mellor, p. 193; R. S. McBride, Jour. Am. Chem. Soc., 34, pp. 394, 415, 1912, Bull. Bur. Stand., 81, p. 611, 1912; W. Blum, Bull. Bur. Stand., 8, pp. 719, 726, 1912; Bur. Stand. Circ. No. 40, 1912.

[2] A thoroughly reliable, certified, standard sodium oxalate is issued by the Bureau of Standards, Washington, D. C., in bottles of 120 and 200 grams. It should be kept in the original bottle, closely stoppered.

[3] McBride and Blum titrate at from 60° to 80°. My preference is for room temperature, because this corresponds to that at which the ferrous oxide is determined, and because of the condensation of steam on the weighing burette over hot water and the possibility of not wiping it perfectly dry before weighing.

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amounts of permanganate are required to oxidize 1 molecule of $Na_2C_2O_4$ (molecular weight = 134) and 2 molecules of FeO (molecular weight = 144), the weight of oxalate per cubic centimeter is to be multiplied by $\frac{144}{134} = 1.0746$, to give the equivalent per cubic centimeter in terms of FeO. This divided by 0.9, or multiplied by 1.1111, will give the value per cubic centimeter for Fe_2O_3.

The solution of permanganate is quite stable [1] if kept out of contact with dust and reducing gases, and especially in the dark. It is best to paint the glass-stoppered stock bottle with black paint, cover the top with a glass cap, and restandardize it every six months. According to Blum the addition of 1 per cent of KOH increases its stability. The sodium oxalate solution does not keep, and must be made up fresh for each standardization.

Potassium Pyrosulphate (1 pound).—This must be free from silica, alumina, and iron. Only the fused salt, that is, the acid potassium sulphate ($KHSO_4$) converted by heat into pyrosulphate ($K_2S_2O_7$), should be used. It should not froth or bubble on melting, due to escape of water. If not procurable it may be made by fusing the acid salt, moistened with a little sulphuric acid, in a platinum basin until there is no frothing and white fumes of sulphur trioxide are given off. The cold mass is broken up, on a stone slab or in a porcelain mortar, but not on an iron plate, into rather small lumps and coarse powder. The sodium salt may also be used, but my preference is in favor of the potassium salt.

Potassium Thiocyanate (1 ounce).—A solution made by dissolving 10 grams in 100 c.c. of water is used for detecting ferric salts.

Potassium Titanofluoride (1 ounce).—This is preferable to titanium dioxide for the preparation of the standard titanium solution, as it is more readily obtained pure. It should be heated at 150° for two hours to render it anhydrous, and kept in a well-stoppered bottle.

Silver Nitrate (1 ounce).—A solution containing 3 grams to the liter is used in the colorimetric determination of manganese. Five hundred c.c. of this may be made up. About 100 c.c. of a

[1] Cf. Mellor, p. 196; Treadwell, p. 603. A standard solution of mine which gave a value of 0.002497 gram Fe_2O_3 per gram on January 12th, gave one of 0.002480 on November 1st of the same year.

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stronger solution may be kept in a small dropping bottle for testing filtrates for chlorine.

Soda Lime (1 pound).—This should be of good quality and granulated.

Sodium Acetate (4 ounces).—This is kept in the solid form.

Sodium Ammonium Phosphate (microcosmic salt). (8 ounces). —This is kept in the solid form and the solution is made as needed.

Sodium Carbonate (2 pounds).—Only the dry, anhydrous salt, of the best obtainable quality, is to be used. A new lot should always be tested,[1] especially for silica, alumina, and iron. I have now abandoned the mixture of sodium and potassium carbonates, formerly recommended and use the sodium carbonate alone.

Sodium Oxalate (4 ounces).—It is important to have this perfectly pure and dry. That furnished by the Bureau of Standards is the most reliable and should be obtained if possible. A bottle containing 120 grams will suffice.

Sulphur Dioxide.—If this is used for the reduction of ferric to ferrous oxide it is better to use the gas, as the solution does not keep well on long standing. The gas may be obtained in 7-pound cylinders, or small quantities of fresh solution may be obtained from time to time.

Titanium Standard Solution.—This should contain 1 centigram of TiO_2 in 10 c.c. It is best made from potassium titanofluoride (K_2TiF_6), which is procurable in a satisfactory degree of purity. The salt should be recrystallized and heated for an hour or two at 150° to render it anhydrous. As nearly as possible 1.5 grams[2] of the anhydrous salt (which contains titanium equivalent to just 33.33 per cent of TiO_2) is weighed out into a platinum dish or large crucible and evaporated four or five times, with 5-gram portions of sulphuric acid (1 : 1), until fumes of sulphur trioxide are given off and almost, but not quite to dryness. All the HF must be expelled. When cool the residue in the crucible is mixed first with 5 c.c. of 1 : 1 sulphuric acid then, cautiously with water, enough sulphuric acid added (if necessary) to make up at least 5 per cent of final volume, and when cool the whole is diluted to 500 c.c. in a measuring flask. Two 50 c.c. portions are diluted

[1] Hillebrand, Bull. 422, p. 40.

[2] Mellor (p. 205, note 4) has made a slip in the figures given in his directions for preparing the solution.

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with a little water and precipitated at a boiling temperature with ammonia water, the precipitate is well washed, ignited and weighed as TiO_2. As iron is a frequent impurity, it is best to bring the two portions of TiO_2 into solution (p. 159) separately by fusion with pyrosulphate and determine the amount of Fe_2O_3 present. This, of course, is to be deducted from the apparent weight of TiO_2. If the standard proves not to contain exactly 0.01 gram of TiO_2 in 10 c.c., it is better to use its actual value in the calculations rather than to dilute it to the proper strength.

The purest titanium dioxide may also be used, 0.5 gram being brought into solution, either by long fusion with pyrosulphate or, better, by evaporation with a mixture of hydrofluoric and sulphuric (1 : 1) acids and subsequent repeated evaporations with sulphuric acid as above. The solution so prepared should always be checked for iron, as the dioxide is more likely to be contaminated with this impurity than the titanofluoride.

The standard solution of titanium keeps well if strongly acid with sulphuric acid (at least 5 per cent), but it is well to determine its titanium content from time to time.

Water.—Only pure, distilled water is to be used throughout the analysis, and it will be understood that this is referred to wherever this substance is mentioned in this book. The use of impure water will vitiate the results of any analysis, and too great precautions cannot be taken to provide for an ample supply of pure, distilled water. This important point is neglected only too frequently. The water, after distillation, should be stored in large bottles of some resistance glass, and should be used as fresh as may be practicable.

Zinc Oxide (1 ounce).—A little of this may be dissolved in ammonia water as needed in the rarely executed determination of fluorine.

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PART III

THE SAMPLE

1. Selection in the Field

Since the object of the chemical analysis of rocks is to ascertain the chemical composition of a body of rock, it is of fundamental importance that the specimen selected for analysis, and the material analyzed, be truly representative of the mass under investigation.

If, for instance, an igneous mass is not uniform in character, and the specimen is selected from some extreme phase of variation, it is obvious that an analysis of this will not give a just idea of the character of the mass as a whole. Again, in analyzing a diorite, for instance, the specimen may be so small or selected with so little care that it contains a larger proportion of hornblende, let us say, than the average of the mass; or the specimen of a quartz-porphyry may carry only a few of the abundant, but readily broken out, quartz phenocrysts and a disproportionate amount of ground-mass. It is evident that an analysis made on such inadequate material, however skilfully it may be executed, cannot represent the true composition of the rock-mass. It is seen, therefore, that the proper selection of the material for analysis depends on two factors: the selection of the representative specimen in the field, the amount of material taken and the proper sampling of this for use in making the analysis.

While the selection in the field is quite apart from the laboratory processes, yet its importance is so great as a preliminary to the analysis that it demands some discussion. This is the more called for since the petrologist will usually collect his own material, for analysis either by himself or by others, and, as has been said elsewhere, "the evidence is conclusive that the specimen analyzed has often been collected with no reference to this point, this fact greatly diminishing the value of the analytical work afterward

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expended on it." In selecting a representative specimen in the field attention must be paid to two points: the uniformity of the mass, especially in regard to mineral composition as well as to texture, and the freshness of the rock.

Uniformity of the Rock-mass.—If, as is true in the majority of cases, the igneous mass is sensibly uniform throughout its extent, specimens should be taken from several parts, when possible, in order to test the uniformity with the microscope. For an analysis representing the composition of such a uniform body of igneous rock, either portions of several specimens from different parts may be mixed, or the analysis may be made on a single specimen, which is considered to be representative of the whole in the judgment of the petrographer, both as decided on in the field and as confirmed by the microscope.

As to the former procedure it may be said that no decisive check of one's results will be possible in the future, and that it is by no means certain that a mixture of several specimens really represents the composition of the whole better than does a single specimen which has been carefully selected with this object in view.

Furthermore, the analysis of a single specimen can be correlated with its mode, or quantitative mineral composition, as determined by the microscope in thin section, and thus both will be available for use in physico-chemical discussion. To put it briefly, the analysis should represent the chemical composition of a specimen and the specimen the composition of the rock-mass, so that petrology and petrography, both in their broader and narrower aspects, may avail themselves of the data.[1]

In all, or nearly all, cases, therefore, and wherever possible, a single specimen should be selected for analysis after due comparison with others from the same mass and consideration of its representative character. The specimen should be taken, if possible, from a mass of rock in place, and not from loose boulders or talus slopes, unless these are the only sources available and it is definitely known that they do come from the mass under investigation.

If the mass is not uniform, but is composed of portions with

[1] The question of the variability of an apparently uniform rock-mass, and the representativeness of a single specimen is briefly discussed in Washington, Prof. Paper, 99, p. 11.

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different characters, such as a composite dike or a stock with marginal facies, representative specimens of the different facies should be collected and an analysis made of each, whether the differences be apparently only textural or those due to mineral composition. If in any way feasible, as close an estimate as the conditions allow should be made of the relative thickness, areas or volumes of each facies. While the possibility of doing this depends to a large extent on the conditions of exposure due to the chances of erosion and denudation, yet it is of such importance in the investigation of certain theoretical questions of petrology that special endeavor should be made to arrive at the facts.

In any case, whether the mass be uniform or composed of several facies, the specimen should be taken, if possible, from some definite locality, one which can be described or named so that it can be readily identified by others, and also one whose accessibility is not likely to be lost through building or other operations. Quarries naturally are especially favorable spots, as fresh specimens are easily obtained, and they are of such a permanent nature as to be readily identified, in most cases, by future investigators. In rapid reconnaissance or exploration one has, of course, mostly to be content with, and often thankful for, chance specimens.

Freshness of the Rock.—The action of atmospheric agencies on rocks may vary from the changes to which Merrill [1] attaches the specific term "alteration," in which "the rock-mass as a whole retains its individuality," but is changed mineralogically, with the production of secondary minerals, chlorite, sericite, zeolites, serpentine, limonite, etc., to those embraced under what Merrill calls "weathering," "involving the destruction of the rock-mass," and its ultimate resolution into sands and clays. The mass resulting from such changes, either of alteration or weathering, can be analyzed by the same methods and with equal facility as can a perfectly fresh rock, but it is evident that the results will not represent the composition of the original magma or unaltered rock body.

While it is true in general that only specimens of fresh (unaltered or unweathered), rock should be chosen for analysis, unless the study of such secondary changes is the object in view, yet it is at times somewhat difficult to decide whether a rock is fresh enough

[1] G. P. Merrill, Rocks, Rock-weathering and Soils, p. 174, 1897.

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for analysis or not. In general it may be said that, for the study of igneous rocks, all weathered specimens are to be rejected, that is to say, those in which the rock-mass has been formally broken down. In the case of alteration, specimens should be rejected where the original color is decidedly changed, as where the rock is of a rusty brown through the abundant production of limonite, or green through that of chlorite. Specimens which effervesce with hydrochloric acid, either cold or on warming, or whose vesicles contain calcite or zeolites, are likewise to be shunned.

Specimens should, therefore, be taken (if possible) from the interior of the mass and not from the surface, and portions of specimens from near the surface, where the rock has been exposed to atmospheric agencies, are to be rejected.

In rocks which appear megascopically to be quite fresh, the microscope may reveal the presence of secondary minerals, the products of alteration, as sericite, chlorite, serpentine or limonite. Although considerable latitude must be left to the judgment of the petrographer in deciding this matter, yet if such minerals are present to any considerable extent, the rock must be regarded as unfit for chemical analysis, unless fresh material is unattainable. This last state of affairs is especially apt to be true of the most basic rocks, such as alnöites, picrites, peridotites, and pyroxenites, which contain a large amount of the easily oxidizable ferrous iron, and of which few perfectly fresh occurrences are known or have been analyzed. For lack of better material, one must often analyze specimens of such rocks that are far from fresh, but the results, while not to be regarded as wholly satisfactory, may yet be of some service.

The results of alteration are usually most clearly shown in the analysis by the figures for H_2O or CO_2, or both. Where these are high the material analyzed must be considered as having been more or less altered, whether this appears in the description or not, with the exception of certain cases mentioned below. While it is impossible to state in exact figures the limits of allowable alteration, until the subject is further studied, it may be held provisionally that H_2O can go up to 2 or 3 per cent and CO_2 to 0.5 per cent, without the rock being considered to be so altered as to seriously affect the value of the analysis. It must also be borne in mind that a rock can be more or less profoundly altered, and yet

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show comparatively low figures for these two constituents, though this is not often to be expected.

The exceptional cases just referred to consist of rocks composed in part of primary minerals which contain either hydroxyl (as muscovite and biotite), water of crystallization (analcite), or carbon dioxide (cancrinite). With rocks carrying analcite, which is the only zeolite that apparently can exist as a primary mineral, the H_2O may amount to 3 or 4 per cent, and yet the mass be to all appearances perfectly fresh, and in some almost certainly so, as Pirsson has shown of the monchiquites. Highly vitreous lavas, as perlites and tachylites, may contain several per cent of water and yet be perfectly fresh; while water often occurs as inclusions, as in the quartzes of many granites. Cancrinite-bearing rocks may have more than 1 per cent of CO_2 and yet be quite unaltered, as far as one may judge from the microscope, so that it is entirely possible, if not probable, that this mineral is a primary constituent in some cases. The existence of calcite as an undoubtedly primary mineral has not been established as yet, though recently, rocks have been described in which its occurrence as such seems to be probable.

In discussing the subject of analyses of altered rocks we may advert to a phase of the matter which is of some importance. When a rock is not fresh it is sometimes assumed that the original composition can be arrived at by deducting the amounts of H_2O and CO_2 and calculating the remainder to 100 per cent. This assumption is generally quite unwarranted, since the processes of alteration are usually by no means simply the result of the addition of the two substances mentioned. On the contrary, they are complex and produce changes of greater or less magnitude in the proportions of some or all of the other constituents. These may be additive, as when calcite is deposited in rocks by means of percolating waters carrying calcium bicarbonate in solution, or they may be subtractive, as when kaolinization of a feldspar takes place with resultant loss of alkalies or lime. In any case it is almost universally true that the processes of rock degeneration affect all or nearly all of the chemical constituents,[1] and that the assumption that such is not true is quite unwarranted by the known facts.

[1] Cf. Merrill, Rocks, Rock-weathering, and Soils, pp. 234 to 240.

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2. Amount of Material

As has been said above, the representative character of the specimen depends, after proper selection in the field supplemented by the use of the microscope, upon the amount of material which is taken for pulverization in preparation for the analysis. The weight of the sample which will adequately represent the average of the rock-mass varies with the texture of the rock, and especially with its granularity, that is, the size of its component mineral particles.

It may first be noted that 10 grams of rock powder should be available for the purpose of analysis, and this amount may be increased to 20 or 30 grams if the analysis is to be very complete, since the determination of some of the rarer constituents demands the use of two or more grams of powder. Indeed, it is always a wise precaution to have 20 grams on hand, in view of the possible necessity for the duplicate determination of some of the constituents, or even the making of a second complete analysis.

It is often impossible to obtain anything like this amount of material, for the analysis of minerals or meteorites and the analyst must be content with smaller quantities, sometimes much less than a gram for the whole analysis. With rocks, on the other hand, there is usually an ample supply, so that the analyst has generally no reason for stinting himself. In this way a number of constituents can be easily determined in separate portions, which could only be accomplished by the use of longer and more complex methods if it were necessary to determine them in a single portion.

The texture of rocks varies within such wide limits that it is impossible to give exact figures as to the amount of material that is representative. Much must be left to the judgment of the petrographer. Speaking generally, and almost without exception, the finer grained and less porphyritic the rock, the smaller will be the amount of material necessary to be representative.

Twenty or thirty grams of chips or fragments will be ample for very fine-grained, aphanitic or glassy rocks, as many basalts, trachytes, and obsidians, especially if they are not porphyritic, or very finely so. With more coarsely granular rocks, such as granites, syenites and diorites, a larger quantity must be taken, depending on the coarseness of the grain. This amount may vary from

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50 grams of a medium-grained rock to 100 or even more if the grain is coarse. In some cases, as in pegmatites, the grain may be so large that only a whole hand specimen, or even several kilograms, will adequately represent the true composition. Very exceptionally the crystals may be of such gigantic size that the relative proportions of the various minerals must be estimated from a flat exposure and corresponding portions of the several minerals weighed out and mixed. Fortunately this last will be rarely necessary, and results obtained thus could be regarded as but approximations to the truth.

If the rock is porphyritic this feature involves the taking of a larger quantity than would be necessary if the grain of the whole were that of the ground-mass. If the phenocrysts are very small, only a few millimeters in diameter, and close together, as in many andesites and basalts, 20 or 30 grams will be sufficient. As they get larger, and if more widely scattered, more must be taken, from 50 or 100 grams to larger quantities. With porphyritic rocks also, care must be taken that brittle or loosely attached phenocrysts, as of feldspar, quartz or leucite do not fall out, so as to yield a disproportionate amount of ground mass in the material for analysis.

3. Preparation of the Sample

Sampling.—If the rock is so fine-grained or so slightly porphyritic that only up to about 50 grams of fragments is considered to be representative, the whole amount, broken up if necessary, may, without sampling, be crushed and ground, as described below.

If, however, the representative amount is much more than this, say 100 grams or over, the final crushing and grinding of the whole will consume an inordinate amount of time, so that sampling is advisable to obtain the smaller amount needed for an analysis that will be representative.

This may be done by breaking up the piece or pieces of rock, if large, with a hammer over a large, clean sheet of paper, until the largest is small enough to be put in the steel mortar. The larger fragments, say down to one-half of a centimeter, in greatest dimension, are crushed, one at a time, to smaller fragments and coarse powder, in the Ellis mortar, and emptied out on the sheet of paper.

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The whole mass is then well mixed with a steel spatula and shaped into a low cone. This is "quartered" with the spatula, and if the quarter is more than about 50 grams, the process is repeated (more than once if necessary) on this, until a proper amount of sample has been obtained.

Methods of Pulverization.—For analysis the sample of the rock must be reduced to rather fine powder, in order that it may be easily and completely decomposed by the reagents used and thus brought into condition for solution. To accomplish this, one of three methods may be followed.

The first is that formerly used in the laboratory of the U. S. Geological Survey.[1] The rock is first crushed to small fragments and powder by means of a hardened steel hammer on a hardened steel plate. The plate is 10 cm. square and 4½ cm. thick. The rock fragment is surrounded by a steel ring, 6 cm. in internal diameter and 2 cm. high, intended to prevent the flying and loss of fragments. After reduction in this way to small particles and powder, the whole is ground down by hand in an agate mortar, in small portions at a time. As will be seen later, the great defect in this method is the unavoidable and probably very serious loss of small fragments and dust, both in the preliminary crushing, which the ring does not wholly prevent, and especially in the final grinding.

The second method is that described by Hillebrand as the one in use in the Survey laboratory.[2] The rock, broken into small pieces, is crushed in an Ellis mortar (p. 41), the pestle being of the knob type. In this it is crushed to a powder fine enough for most of the portions used for the analysis. When the decomposition calls for a finer powder, small portions are ground down by hand in an agate mortar; the material may be sifted. The use of mechanical grinders has been abandoned in the Survey laboratory.

In the third method, which is the one I have followed for many years, the rock, broken into small pieces, is crushed in a hardened-steel mortar much as in the Survey method but a light hammer is used. After the first crushing of the whole, it is sifted through silk bolting cloth, the oversize being again crushed and

[1] Hillebrand, Bull. 176, p. 31.
[2] Hillebrand, Bull. 422, p. 46.

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sifted, and this operation is repeated until only a gram or so of oversize portion remains, which is ground by hand in an agate mortar.[1]

In considering the relative merits of these methods, two factors must be discussed, as on them depends the attainment of the object in view, namely, the production of a rock powder that will represent as accurately as possible the composition of the rock specimen taken. These two factors are: contamination from the mortars, and the loss caused by the flying off of fragments and dust.

Contamination by iron derived from the steel mortar and pestle or plate and hammer is likely to be more serious than that by silica derived from the agate. This is because, in nearly all igneous rocks, silica is present in much greater amount than are the iron oxides, and the introduction of metallic iron would affect the ratio of ferrous or ferric oxide. Furthermore, I believe that the liability to contamination by iron is more likely to be relatively greater than that by silica, in spite of Hempel's experiments.[2] My first hardened steel "diamond" mortar (not made by Ellis), shows greater signs of abrasion, though it is but slight, than my small agate mortar, though both have been in use concomitantly for the same period of over twenty years, the latter indeed some years longer.

If the steel is properly hardened, and the crushing done by strictly vertical blows, the contamination by iron through abrasion, is slight, so slight indeed as to be negligible.[3] There is, however, a very slight contamination, especially on long-continued crushing, even though this be properly done, as Hillebrand shows. In any case, this source of error would seem to be unavoidable. The rock must be reduced to powder for analysis, and hardened steel is at present the only practicable material of which to make the mortar.[4]

It is essential, and most important to remember, that there must be absolutely no rubbing or rotary motion of the pestle

[1] Hillebrand (p. 52) has made a slight slip in his description of this method. Only the last, small portion of oversize material is ground down in agate, not the whole amount of powder, as he states.

[2] Cf. Hillebrand, Bull. 422, p. 56.

[3] Cf. Hillebrand, Bull. 422, p. 51.

[4] Osmiridium and tungsten would seem to be out of the possibility of general realization.

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during the crushing. Any such motion will inevitably introduce iron into the specimen.

Contamination by silica from the agate is very slight. It is quite negligible if the grinding is not long continued. Experiments by Allen,[1] in which 200 grams of quartz sand were ground for 19.5 hours in an agate mortar, showed a loss by abrasion to the pestle and mortar amounting to .1455 per cent of the quartz. With small amounts and with only a few minutes grinding the contamination is certainly negligible.[2]

In my opinion the use of mechanical grinders is to be avoided. Apart from the cost, the danger of contamination by oil or metal is always present, in spite of safeguards. Furthermore, the long-continued grinding for which they are used is not only unnecessary for the whole of the sample, but introduces, besides silica, the possible errors of oxidation of the ferrous oxide (p. 183) and the adsorption of water by the fine powder.[3] Water, on the other hand, may be expelled from hydrated minerals,[4] and carbon dioxide from calcite,[5] by long-continued grinding.

If the rock is sensibly homogeneous, like an obsidian or a very fine-grained basalt, the loss of fragments incidental to crushing or to the grinding of a coarse powder will not materially affect the composition of the final material. If, however, the rock is visibly non-homogeneous, phaneric or porphyritic, the change in composition so caused may be serious. The tough minerals, such as pyroxene and amphibole, crush less readily but, when broken, they tend to fly more than the less tough ones, such as quartz, feldspar, nephelite, or leucite, or glass. If not confined they will be lost in part, and will also, in their flight, carry away or drive out some of the surrounding powder, which would consist in greater part than they, of glass, quartz or feldspathic minerals.[6]

[1] Hillebrand, Bull. 422, p. 56.

[2] The estimate of about 0.3 per cent of silica introduced, as given by Connor (XII Cong. Geol. Int., C. R., p. 885, 1914), is surely higher than in my experience and may be due to special conditions.

[3] Cf. Day and Allen, Carnegie Publ., No. 31 p. 56, 1905; Hillebrand, Bull. 422, p. 64. E. T. Allen has found that optical glasses, on long-continued grinding in a mechanical grinder may absorb as much as 1 per cent of water.

[4] Hillebrand, Bull. 422, p. 64.

[5] Johnston and Niggli, Jour. Geol., 21, p. 614, 1913.

[6] The influence of hardness or brittleness on change in composition during

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It is not known by experiment in what direction such losses would tend. Indeed, from this cause, the tendency to greater loss in either direction would probably be irregular and dependent on the different mineral and textural characters of the rocks. In either case flying fragments would, however, tend to introduce an error in the composition of the final material.

The loss from dust blown or drifting away in the air must also be taken into consideration. This will, almost certainly, be more largely made up of salic than femic minerals, because of the greater brittleness and lower specific gravity of the former.

In the first method above, the contamination by iron would probably be notable, and, what is a still more serious matter, the loss by flying fragments, as well as by dust, is obviously apt to be so great that the method should be abandoned, as it has been.

The second method involves prolonged crushing in the steel mortar to bring the whole powder to a state of fineness (something like 25 meshes to a centimeter) that will permit ready attack by sodium carbonate. This renders the sample liable to contamination by iron in direct ratio to the time expended in crushing. If the crushing is not carried out to this extent, but if the powder yielded by the steel mortar is ground down in agate, loss and consequent change in composition by flying fragments would be inevitable, as is evident from the considerations above and as can be easily verified.

In the third method the crushing in the steel mortar is briefer than in the second, because the larger fragments are separated by sifting from the powder, and thus in the subsequent re-crushings are not protected by the cushioning effect of this and are therefore more quickly pulverized.[1] The sifting, if carried out in a quiet place, free from draughts, and over a large sheet of paper,

pulverization has been incidentally studied by S. Zaleski (Tsch. Min. Pet. Mitth., **14**, p. 347, 1895). Working with granites, he found that the coarser portion of the powder was higher in silica than the finer, due to the greater hardness (and less brittleness) of the quartz. See also I. A. Williams, Amer. Geol., **35**, p. 89, 1905.

[1] I have not succeeded in getting any indications of the presence of metallic iron by grinding under water in an agate mortar, as described by Hillebrand (p. 51, note) the powders obtained by my method. The samples (of rocks that had been previously analyzed) included various kinds; granite, diorite, norite, trachyte, phonolite, andesite, and basalt.

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involves a negligible loss of dust. This can also be entirely done away with if the double glass box be used (p. 45). The grinding of the small amount of coarse, final portion in agate takes but a short time, not five minutes in all.

The objection against the use of silk bolting cloth [1] is of little moment. The danger of contamination by particles of silk, and hence of error in the determination of FeO, is more theoretical than real, and is certainly less than the errors inherent in the determination itself. If the powder from the mortar be only shaken, not rubbed, through the sieve, only a negligible amount of silk in all would pass into and would be distributed through twenty or more grams of rock powder, of which but one-half a gram is taken for the FeO determination. It is certain that the reducing action of the extremely small amount of organic matter thus possibly present would be very much less than that necessary to decolorize a single drop of the permanganate solution used, and hence would be entirely negligible, even for the most accurate work.

Metal sieves should not be used in the analysis of rocks or minerals, as they might introduce serious contamination or complication in accurate work.

It is, therefore, held that the third method is the one least liable to error and the one which will presumably furnish material for the analysis that will more closely represent the original rock than the second, and still more than the first. It may now be described in detail.

Pulverization of the Sample.—The whole amount of the sample which is representative of the rock-mass is reduced to small fragments, if the amount of material is small, by breaking up with a hardened hammer on the top of the steel pestle which is placed in position in the mortar. Care must be taken to avoid the flying off of fragments.[2] If the pieces of rock are broken on the pestle-head they can be held in the dry fingers and cracked by a sharp, quick blow, and the pieces so obtained cracked again. The largest

[1] In Bull. 422, p. 51, Hillebrand advocates its use in sifting, if this be necessary.

[2] Wrapping the rock in paper for the first breaking up, as is sometimes done, is not to be recommended, as it is almost impossible to free the fragments entirely from adhering paper, and the considerable organic matter thus introduced will lead to serious error, especially in the determinations of FeO and H_2O.

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of the fragments finally obtained must be small enough to drop easily into the mortar, and all of them, with any resulting small grains and powder, are placed on a clean sheet of white, smooth paper.

One of the small fragments of rock is then placed in the steel mortar, which rests on a firm, solid support, preferably an upright, solid block of wood, resting on the floor, and is partially crushed by a dozen or so sharp but gentle blows of a light (one-half pound) hammer. The pestle is removed and placed on the sheet of paper, and the contents of the mortar are dropped into the glass box, from which the gauze and brass ring have been removed. A few gentle taps of the base of the mortar against the cylinder assist in removing the last portions of adhering powder from the cavity. It is well to break up any coherent lumps of fine powder in the glass box by gentle pressure with the pestle, as this will aid in the subsequent sifting.

It is absolutely essential, as pointed out above, that there should be no rubbing or grinding motion during the crushing. The pestle and cylinder are held firmly in the fingers of the left hand, so that there may be no rotary motion, and the blows of the hammer should be gentle and strictly vertical. Any grinding of the pestle against the sides of the cylinder or rotation on the rock powder will surely introduce some iron through the wearing of the metal surface.

The whole of the fragments and powder resulting from the first crushing are to be thus passed through the mortar and placed in the box. The cylinder should not be filled more than to the depth of from 3 to 5 mm. at a time, and it is not necessary nor advisable to crush all of the rock to a fine powder at this stage. Care should be taken that the cylinder is placed vertically in the base before any fresh material is placed in it, and that the pestle is also inserted in a strictly vertical position. Lack of attention to these points gives rise to the danger of small shavings or chips of steel being cut off and falling into the rock powder.

When all the sample taken has been thus partially and coarsely pulverized and placed in the glass box, a piece of the silk gauze, about 10 or 12 cm. square, is stretched over its mouth and held firmly in place by the brass ring which is slipped over it. If the double form is used, the second box is also

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put in place. The sieve is then held upside down over another sheet of white, hard-calendered paper,[1] about 300 by 400 cm. (12×16 inches), a short distance above it, and gently shaken from side to side. The paper is, of course, not needed if the double box is used. This operation should be conducted as gently as is consistent with proper efficiency, and in a place free from draughts, so as to avoid loss of dust.

When no more powder falls through, the brass ring and the gauze are removed, and the contents of the box are poured out on the first sheet of paper. The whole process of crushing in the steel mortar is then gone through with on this material, exactly as before, and it is again sifted. The residue from the second sifting is again treated, and if necessary the process is repeated till only a small amount (1 or 2 grams) of coarse powder is left in the glass box, too coarse to pass through the gauze. This will ordinarily take about three or four successive crushings. This final portion is then ground down by hand in the agate mortar in small portions at a time, the different portions as they are ground being scattered over different parts of the low heap of powder on the sheet of paper, or in the second box. Unless the amount of material to be crushed is very large, or the rock extremely tough, three or four successive crushings will be all that will be needed. The final grinding of the last small lot of powder should never be omitted, as this consists of the tougher minerals of the rock, and if it were thrown away, the correspondence between the sample and the rock would be incomplete.

When the whole is thus passed through the sieve, the powder is very thoroughly mixed. This is best accomplished on the paper by tilting up successively the ends and the sides of the paper until the mass is in the center. One end of the sheet is then raised gently until the heap of powder is lifted and turned over and slid toward the other end. It is essential to proper mixing that the mass of powder should not only slide down, but that it should actually be turned over. This is repeated many times, not only from end to end but from side to side, with an occasional oblique roll. A platinum spatula may also be used to mix the powder, care being taken that none of the paper surface be rubbed off, but the process described above is to be preferred. When it is con-

[1] The sheets used by botanists for herbaria will be found convenient.

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sidered that the powder is thoroughly mixed, it is not an undue precaution to roll it over in different directions several times more. The powder may also be quickly and thoroughly mixed by putting it again in the box and sifting it through a somewhat coarser gauze, best into the second box.

After thorough mixing, the powder is poured into a specimen tube. For amounts of 20 to 30 grams, one $6\times\frac{7}{8}$ or $5\times\frac{5}{8}$ inches will answer, while one of $4\times\frac{1}{2}$ inches will hold about 10 grams of rock powder. The tube used must be carefully cleaned, inside and out, by washing first with distilled water, then with a little alcohol, and thoroughly dried. This is accomplished by the application of a gentle heat, the moist air being at the same time sucked out through a piece of glass tubing attached to a suction-pump. The tube must be perfectly cool before the powder is introduced, and is closed with a smooth, well-fitting cork, on the top of which the number of the specimen is written in ink. The number, name, and locality of the specimen should also be written on a small label pasted on the side of the tube.

In order to avoid possibility of rusting, the steel mortar should be cleaned, a stiff brush and a dry cloth being used, as soon as possible after the preparation of the samples, and placed in a tightly closed box. The bolting cloth may be used many times, but it must be very thoroughly dusted free from any trace of rock powder, after each operation. For the most accurate work a fresh piece is to be taken. The glass box or boxes and the brass ring are also to be cleaned.

It is of the utmost importance that *all* of the sample which is prepared for the steel mortar, either the chips if the amount of material be small or that obtained by quartering if it be large, be pulverized and passed through the sieve or ground in the agate mortar. If it is only partially pulverized and the last portions are rejected, it is clear that the powder so obtained will not represent the average composition of the rock. The rock-forming minerals differ widely in brittleness, so that the portions pulverized first will have a content higher than the average in particles of the more easily pulverizable minerals, as quartz, feldspar and feldspathoids, while the last portions will be especially rich in the tougher minerals, pyroxene, hornblende and the micas.[1] The micas, above all,

[1] Some data are given by I. A. Williams, Amer. Geol. **35**, p. 38, 1905.

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are difficult to pulverize completely either in the steel or agate mortar, on account of their ready cleavage and flexibility, but the thinness of their flakes render these quite easy of attack by the reagents used. If they are present in any quantity it is necessary to see that the flakes are well distributed through the powder.

The analysis should always be carried out on air-dry powder, as specially dried rock powder invariably reabsorbs some or all of the lost moisture by exposure to the air during the weighing and whenever the tube is opened, or even in time if it be closed.[1] This absorption of water is the greater the finer the powder, and the amount of water thus absorbed has been shown by Day and Allen[2] to be of the same order of magnitude as that of the "hygroscopic" water observed in the analyses of feldspars and many rocks free from hydrated minerals. The preparation of the sample should, therefore, be undertaken on a dry day; never during rain.

[1] Cf. Hillebrand, Bull. 422, p. 65.

[2] Publ. Carnegie Inst., No. 31, 1905, p. 57; and Am. J. Sci., **19**, 1905, p. 127.

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PART IV

OPERATIONS

1. Preliminary Observations

In the chemical laboratory, above all places, is "cleanliness next to godliness." The analyst must be scrupulously particular about the freedom of the laboratory from dust and dirt, and about the cleanliness of his apparatus. No matter how clean the laboratory may be, all vessels whose contents are to stand for more than a short time, and especially over night, must be covered to prevent the entrance of dust.[1] In prolonged evaporations it is well to protect the liquid by a large pane of glass or a Meyer's evaporating funnel held above the basin by a clamp and support reserved for this purpose.

The deposit of ammonium salts that accumulates on the bottles standing on the shelves is not only unsightly, but is a constant possible source of contamination. The bottles should, therefore, be wiped off every now and then, and the work-bench also washed occasionally.

Every glass utensil or other soiled piece of apparatus should be washed clean and wiped dry immediately after using, and put away in its proper place. This applies especially to beakers. By conforming to this rule soiled vessels will not accumulate, and there will be no danger that they be put away and used inadvertently in place of clean ones.

A clean beaker is to be used to receive a filtrate, even if this is to be rejected, so as to permit the recovery of the precipitate if it passes through the filter or if the latter breaks. Before using a clean beaker or flask, it should be rinsed out with a little distilled

[1] A beaker is covered with a watch-glass, of a size so that the edge projects about 2 cm. around the beaker, and is placed convex side down. A flask is best covered with a small beaker, turned upside down.

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water from the wash-bottle. In volumetric or colorimetric work the burette should be rinsed out with a little of the solution to be placed in it, even if it is apparently dry.

The student should shun all slovenly manipulation, such as spilling liquids or solid reagents on the work-bench, or letting liquids drip when pouring from the bottle. Tobacco ashes are a constant source of danger, though the author must plead guilty to running this risk constantly. The wearing of an apron in making a quantitative analysis is to be deprecated, as tending to confirm one in slovenly habits. If the analyst is liable to drop acids on his clothes he is more than liable to spill some of the solutions he is analyzing.

Every beaker, flask, crucible, or other receptacle that contains a precipitate or filtrate obtained in the course of the analysis and that has to be laid aside temporarily should be clearly labelled with the number of the analysis and the name of the substance. Otherwise confusion or uncertainty is almost sure to follow, especially if a complicated analysis or a series of analyses is in progress. The labelling can be done by placing a piece of paper with the requisite data on the cover glass or by writing on the spot of ground glass on the side of the beaker or flask.

The beginner has a marked tendency to over-carefulness in some details of the analysis. This excess of zeal is expressed in using utensils of sizes that are much larger than are needed, in using inordinate amounts of precipitant, of wash water, in igniting precipitates for a much longer time than is necessary, or in using a much too high Bunsen flame. This tendency is so pronounced that the beginner in analysis should be on his guard against it. It is to be discouraged because it not only greatly lengthens the time needed for the analysis but, which is more serious, it tends to lessen the accuracy of the work through the solution of precipitates and for other reasons.

The beginner should take full notes during the progress of the first analyses, until the various methods become familiar, and even then all occurrences or manifestations out of the ordinary are to be noted and not left to the memory. The details of all the calculations are to be recorded in the note-book for future reference. It may sometimes happen that an apparent analytical error or an unsatisfactory summation is merely due to a slip in

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arithmetic, and a re-examination of the recorded weights and calculations may obviate the necessity of a duplicate analysis.

In rock analysis a preliminary qualitative examination is seldom, if ever, necessary. The microscope will often serve the purpose. But if not, and if the presence of some unusual substance is suspected, it is better, as Hillebrand remarks, to assume its presence and conduct the quantitative analysis on this assumption. This will be time saved in the end, even if the result is merely to prove the absence of the suspected body, which in itself may be a fact of some interest. In such cases, one should always test by qualitative methods the character of the weighed precipitate to see whether it is really the substance in question or not.

Finally, before beginning an analysis the student should see that the balance is correctly adjusted, and that all the necessary apparatus and reagents are at hand, so that the work may proceed without interruption. It will be well to read the whole of the description of each of the various operations and methods before beginning their execution, as some information may be given at the end which is essential to the proper performance. Thus, in the determination of combined water, if the rock which is being analyzed contains haüyne or sodalite, and the whole description of the method has not been read, the student may be unaware of the necessity for retaining the chlorine or sulphur trioxide, and so will obtain erroneous results.

As illustrative of the precautions that must be taken in highly accurate work, it may be of interest to the student to read Richards' discussion of the Methods Used in Precise Chemical Investigation.[1]

In subsequent pages some of the most important analytical operations are described in considerable detail, and it will be well for the beginner to read them before, and consult them during, the making of the analysis.

2. Sources of Operative Errors

The distinction between errors that are incidental to operations and those that are inherent in the methods used will be discussed later (p. 119). It may be useful here to give a list of those

[1] T. W. Richards, Determinations of Atomic Weights, Carnegie Institution Publication, No. 125, p. 97, 1910.

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sources of error that are connected with the various operations which are more serious in their consequences or which may be most often met with by the student, and which should be more particularly guarded against.[1] The precautions that may be taken against some of them are given in connection with the descriptions of the various operations.

This list is so long and formidable in appearance that the beginner may be disheartened by the prospect of continuous vigilance that confronts him. For his encouragement it may be said that their aggregate number is more serious in the seeming than are in reality the occurrence or possible consequences of many of them. The only ones that are really inexcusable at the beginner's stage are those arising from carelessness, and these may soon be overcome by proper attention and thought. The great majority of the others will readily be avoided or overcome by the attentive and conscientious student, who, not only follows the conditions and precautions mentioned in the various descriptions of operations and methods, but who also looks upon the analytical work with intelligent interest, and consequently does not "learn nothing more than to follow directions." To such a worker the very sources of error themselves are of interest, stimulating him to constant attention, and lending to the progress of the analysis an element of interest and something akin to excitement that it would lack if every operation and method were wholly free from possible error.

Sampling.—Correct sampling is of fundamental importance, but this must be considered as a preliminary to the analysis.

Unfavorable Conditions.—The laboratory may be in a dusty location, or not kept in a properly neat and clean condition; the laboratory air may be contaminated by fumes; machinery in motion may disturb the balance readings; the ceiling may be of such character or in such condition as to drop particles into vessels beneath; a window facing the sun, or some other source of heat, may affect the balance; the exterior light surroundings may be such (brick walls or foliage) as to disturb colorimetric readings; the air may be so damp that powders or objects to be weighed absorb a disturbing amount of moisture· the attention may be distracted by interruptions or noise.

[1] Mellor (p. 249) gives a similar but shorter list.

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Personal Equation.—There may be personal peculiarities in the reading of burettes and other instruments that lead to constantly high or low results; there may be a peculiarity in color perception that tends to constant high or low estimates in colorimetric determinations; one eye may perceive colors differently from the other; impatience may lead to the undue hastening or shortening of operations;[1] overwork may cause fatigue and consequently lead to many opportunities for error; the need for quickly attained results may cause errors of many kinds; the analyst may not be in good health.

Apparatus.—The balance may not be properly adjusted; one arm may have been lengthened by heating from a window, etc.; the zero point may not be known, and it may be distant from the center of the scale; the weights may not be correct; the measuring flasks and burettes may not be consistent with each other; the glass of which the beakers are made may be too readily attacked by reagents.

Impure Reagents.—The impurities found in reagents are of great variety, and some of them quite unexpected. It is not practicable or necessary to enumerate them.

Standard Solutions.—The standard solutions of permanganate, titanium, and manganese are liable to change and deterioration with lapse of time; they may change by evaporation through opening the bottle or pouring them out; their titer may be increased by not shaking the bottle previous to use, or lessened by moisture in the burette.

Numerical Errors.—The position of the rider on the beam, the weights, the position of the meniscus in the burette or that of the mercury in a thermometer, may be incorrectly read or noted down; an incorrect factor or an incorrect figure from a table may be used in calculations; arithmetical mistakes may be made in the calculations; the summation of the results of the analysis may be incorrect.

General Sources.—Volumes may not be corrected for temperature conditions; platinum crucibles may lose weight on ignition; liquids may be contaminated by solution of the material of the containing vessel; precipitates may be contaminated by other substances that are carried down with them in the precipitation;

[1] This might come more properly under the head of carelessness.

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liquids or solids may be contaminted by absorption of fumes or gases (as carbon dioxide or ammonia) from the atmosphere; sulphur may be introduced from the burner gas or from rubber stoppers; platinum may be introduced during fusion in crucibles or evaporation in basins of this metal; copper may be introduced from copper utensils.

Inexperience.—Errors due to this source may be very serious. but they are generally less harmful than those caused by carelessness, and they should soon be overcome with practice and attention.

The most common and persistent source of error due to inexperience is the tendency to bigness and the overdoing of things. A too large size of vessels, such as beakers, adds to the difficulties of manipulation, increases the volumes of wash water and other liquids, tends to the over-washing of precipitates, and increases the time taken for the analysis; the use of too large filters tends to the over-washing of precipitates and the under-washing of the filter; the volumes of wash liquids or the amounts of precipitants are easily made much larger than is needed or desirable, and this greatly increases the chances of error in many ways; the use of too large flames may lead to reduction of the substance ignited or loss by draughts, and it also wastes gas and makes unnecessary noise; the over-washing of precipitates leads to their partial solution and to too low results; too prolonged ignition may cause undue loss of weight of the crucible, change or loss of weight of the ignited substance, and always loses time.

Insufficient washing, or cessation of ignition before constant weight has been attained, lead to too high results; improper position of the crucible as regards the flame, especially that of a blast, may cause loss; the loss of molten substances, such as of the carbonate fusion, by spattering, or of the pyrosulphate fusion by spattering or by " creeping," will cause low results.

Among other sources of error are the reading of a burette before all the liquid has run down the wall; the loss of precipitate by " creeping " up the sides of a beaker or funnel; the incomplete removal of a precipitate from the sides of a beaker; effervescence on the addition of acids to carbonates (as in the solution of the carbonate cake) or that of strong ammonia water to hot or acid liquids; incomplete reduction of ferric oxide by not passing

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hydrogen sulphide for a sufficient time or the partial oxidation of ferrous oxide by faulty manipulation; the throwing out of precipitate by incautious application of the jet; and an improper manner of introducing reagents or precipitants.

Carelessness.—The errors due to this cause are the least excusable and are generally the most serious as well as the most easily avoided. They include: Injury to the balance or weights by improper handling; placing hot or damp objects on the pan; the spilling of liquids or powders during transfer; the loss of liquid by splashing or " bumping," or of powder by draughts of air or by their " puffing up " on the addition of liquids; the use of dirty utensils and an untidy or dirty work-bench; the dropping or breaking of vessels; the ill-treatment of platinum crucibles, so that they become dented or otherwise injured; laying the stoppers of reagent bottles on an unclean surface, such as that of the work-bench; the absence of a cover glass on a beaker during boiling, or that of the crucible cover during a fusion or ignition; the incorrect labelling or not labelling the various precipitates and filtrates; inattention to operations in progress, not washing used vessels as soon as possible and putting them in their proper places; and not following the given directions closely.

3. Weighing [1]

Preliminary Remarks.—The object to be weighed should be perfectly dry, so far as its surface goes, as damp objects will not only give incorrect results but will injure the pan.

The object should always be at the temperature of the room. Nothing hot, or even warm, is ever to be placed on the balance pans. Apart from possible injury to and staining of the pan, the air currents set up by a warm object may buoy up, so to speak, the arm of the beam, thus making the weight apparently less than it really is; or the heated air may expand the arm and thus give an apparently too great weight. On the other hand the object should not be colder than the surrounding air, because of the liability to the condensation of moisture on it.

No solid reagent of any kind, whether in the form of powder

[1] Fresenius, **1**, pp. 21–25; Gooch, pp. 14–24· Mellor, pp. 7–27· Morse, pp. 8–22; Treadwell, **2**, pp. 8–18.

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or not, is to be placed directly on the pan. Such substances should always be placed in and weighed with some receptacle, such as a crucible, watch glass, or weighing tube or bottle.

The object to be weighed should always be placed (for a right-handed person) on the left-hand pan, and the weights on the right-hand pan. This rule is to be strictly adhered to, as it eliminates error due to inequality of the balance arms (Mellor, p. 22).

When weighing a crucible that weighs, for example, 19 grams, it is a great temptation, in order to save time and labor, to put the 20-gram weight on the right-hand pan and a 1-gram weight on the left, with the crucible. Although this procedure may be adopted by the experienced analyst, who knows his crucibles, and for the gram weights only, it should be avoided by the student, as it is very likely to cause confusion and error in noting the weights. Above all, it should never be done with the decigram and centigram weights, where the practice is almost sure to cause error.

The object to be weighed, as well as the heavier weights, should be placed at the center of the left- and right-hand pan, respectively. This will prevent the sometimes violent swinging of the pan that occurs when a heavy mass is placed near its edge, and which may be difficult to stop. Large and irregularly shaped objects, such as a weighing burette, are to be suspended from the hook above the pan, and a tube is best supported on a light metal frame to prevent rolling.

The pans should not be allowed to have any rotary or swinging motion, as this may cause injury to the knife edges. If either pan swings on release, the motion should be stopped by gently raising the pan arrest so as to stop the pan at the middle of the swing. On full release, during the observation of the pointer, the pans should hang vertically and with no swinging from side to side.

The weights and crucibles, or such objects, should be handled only with the ivory-tipped forceps, and should be placed on and removed from the pans very gently. Indeed, all motions involved in weighing should be gentle and slow. No weight, not even a centigram one, is to be dropped on the pan.

Both the beam and pans are to be arrested before placing anything on, or removing anything from, the pans. The motion in arrest and release should be very gentle and gradual, and the beam should be arrested only when the pointer is at, or at most not more

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than one division from, the zero point. The balance should never " chatter " through arresting the beam too quickly. These rules are very important, and neglect of them will inevitably lead to speedy impairment of the balance's accuracy.

The balance case is left open while putting on the weights down to, and including, the lowest needed from the box, but is to be closed during the weighing with the rider for milligrams and tenths.

The observer should sit directly in front of the center of the balance " so as to avoid errors due to parallax in reading the pointer." It should be seen that the balance is level and, if necessary, it is to be adjusted to horizontality by the levelling screws and the plumb-bob or spirit-level that should be part of the balance case equipment. The rider, supported on its hook, should be so far above the beam that there is no possibility of the beam hitting it.

If the zero-point has not been recently taken, or if it is unknown, it should be determined before a series of weighings. It is especially important to determine the zero-point if the balance is at the disposal of several persons or is in general use. Carelessness with the balance is far too frequent.

To determine the zero-point, the beam of the empty balance is gently released, and if it does not swing it is set to swinging slightly by a little puff of air from the rubber bulb (p. 29), or by waving the hand gently near one of the pans, great care being taken not to touch this. The swings should not be more than ten divisions on either side of the center of the scale. The balance case is then closed and, after two or three swings, the divisions on either side of the center at which the pointer stops and turns back are recorded, tenths of a division being estimated, best with the reading glass. Note two or three swings to the left and a number one greater than this to the right. Take the mean of the left and right swings. Add these together, divide by two, and subtract the quotient from the greater of the two mean swings. The difference is the zero-point, that is, the distance from the center of the scale at which the pointer would stop, either right or left, if the beam were allowed to come to rest.

If the zero-point is within one division of the center on either side, the weighing may be carried out on the assumption that the zero-point is the center of the scale, as the balance should be so

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adjusted that one division corresponds to one-tenth of a milligram, which is the limit of weighing. If it amounts to one or two divisions this zero-point is to be taken as the center-point of the swings in weighing. If it is three or more divisions from the center, and if the balance has been dusted carefully, the balance should be adjusted so as to bring the zero-point near the center of the scale by very cautiously moving one of the screw weights at the ends of the arms.

In ordinary analytical work there is no need of adopting such refinements as correcting for the buoyancy of the air, or such accurate, but time-consuming, methods of weighing as those of Gauss or Borda. The usual method by swings is used.

Process of Weighing.—The object to be weighed, if it is a crucible, should be ignited at a bright red heat for a few minutes, placed in the desiccator when it has cooled to below visible redness (never when red-hot), and allowed to cool to room temperature before being weighed. This will take ten minutes or so with platinum but much longer with porcelain. The object of the ignition is to bring the crucible into the same condition that it will be in after the ignition of the precipitate. If the object cannot be ignited, but is dried in the oven, it is placed in the desiccator immediately after removal from the oven and allowed to cool to room temperature. A specimen tube, weighing burette, weighing bottle, or absorption tube, is to be wiped with a dry and clean cloth. Such objects may be handled lightly with the tips of the dry fingers, which will remove any electrification caused by the rubbing.

After having made sure that the pans and beam are arrested, the object to be weighed, say a crucible, is placed on the center of the left-hand pan, and weights approximately equal to that of the crucible[1] on the right-hand pan. The pans are released very gently and if they swing they are to be stopped as described above. Then the beam is very slowly and slightly released, the direction of movement of the pointer is noted, and the beam and pans are again very gently arrested. If the weight on the right-hand pan is too great, the smallest weight is removed, or if it is too small the next larger weight is added; then the pans and beam are

[1] It is convenient to have in the balance case a small card on which are written the numbers and weights of the different crucibles in use.

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released and the pointer is observed as before. The process is continued in this way, adding or removing the weights *systematically*,[1] and not at random, until no more weights need be put on the pan, and until 10 milligrams, measured with the rider on the beam, moves the pointer to the left, in other words, is too much.

The balance case is now closed and the weighing is finished with the rider. This should also be carried out systematically; for example, by beginning with the rider at the center of the beam and moving it successively smaller distances. When the weighing gets down to tenths of a milligram (small beam divisions) the extreme excursions of the pointer are to be noted. The tenth-milligram is regarded as final that gives a zero-point the same as that of the empty balance, or when the swings are equal on both sides of the center of the scale if the zero-point is only one or two divisions away.

The beam is swung or set in motion during these final observations by using the rubber bulb or by lightly waving the hand up and down near one pan, taking care not to touch this.[2]

In entering the weights in the note-book, it is best done systematically and uniformly, by first noting down the weights from the vacant spaces in the weight-box, and then checking up as the weights are removed from the pan and replaced in their proper places in the box.

As Fresenius points out[3]: " The student should from the commencement make it a rule to enter the number to be deducted in the lower line." The entry in the note book should, therefore, be in this form:

Cruc.+subst.	=33.0909
Cruc.	=32.0712
	1.0197

[1] The weights should not be placed one on the other, but should be laid down alongside each other and in order from heavier to lighter; this will facilitate the checking up of the weight and diminish the possibility of error in replacing the weights in their proper places in the box.

[2] The beam can also be set in motion by placing the rider on the beam for an instant, or by a " trick " in releasing it; but these should not be tried by the beginner.

[3] Fresenius I., p. 21.

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The uniform adoption of this procedure will lessen the possibility of annoying arithmetical mistakes.

When the weighing is ended, it should be seen that the pans are empty and free from dust or specks, the balance case is closed, the rider lifted from the beam, and the weight-box closed, so that all will be safe from dust and immediately ready for another weighing. The practice of leaving weights on the pan, as during the ignition of a precipitate, which is simply to save the slight trouble of taking them off and putting them on again, is very injudicious. It is one of the small things that marks a person who does not appreciate the fundamental importance of the balance.

A word may be said of the practice of so-called "rational" weighing; that is, the weighing out of an exact amount of substance so that the weight of a precipitate will express immediately the percentage of a constituent. Thus, if exactly 0.5308 gram of a substance that contains Na_2O but no K_2O is weighed out, the weight of the NaCl obtained will be the percentage of the Na_2O. This is because the weight of the NaCl is multiplied by .5308 to reduce it to Na_2O, and dividing the product by .5308 (the weight of substance taken) to get the percentage will, of course, yield a quotient identical with the weight of NaCl. An example will be found on p. 246.

The only purpose of such weighing is to avoid calculation, and generally laziness here defeats its own object. The mental labor involved in the calculation is very slight, indeed less than that involved in the exact weighing, while the latter generally consumes far more time. For both reasons, but especially because of the loss of time, the practice is not commended.[1]

4. Decomposition[2]

After the portion of rock powder is weighed out it must be decomposed, either by fusion with a flux or treatment with acid, so as to bring it into solution preliminary to analysis.

[1] Cf. Mellor, p. 54.

[2] A mild protest may here be registered against the phrase "opening up," used by some English chemists, instead of "decomposition." The former suggests rather getting at the contents of a tin of sardines or removing an obstinate oyster from its shell than getting a mineral into proper condition for analysis.

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A number of minerals, such as leucite, nephelite, and olivine, are easily and completely decomposed by hydrochloric acid, and their analysis may be effected after such a simple preliminary solution. Others again, such as quartz, orthoclase, albite, pyroxene, and hornblende, are either quite unattacked or only partially decomposed by this medium. Since practically no igneous rocks, so far as we know, are composed entirely of the first class of minerals and are completely soluble in hydrochloric acid, it is necessary to bring their constituents into soluble form by other means, as a preliminary to their analysis.

A number of methods have been proposed for this purpose, some of them based on the use of hydrochloric, sulphuric or hydrofluoric acids, and others involving the use of various fluxes, as alkali hydroxides, carbonates or fluorides, calcium carbonate, lead or bismuth oxide and boric acid. A description and discussion of these is given by the authors cited below,[1] but it is unnecessary to enter into this phase of the matter here. It will suffice to describe only those methods which commend themselves to the author and to the chemists of the U. S. Geological Survey, and the use of which is recommended in this book.

In order to determine the different constituents of a rock, different reagents and methods of decomposition are found to be appropriate, depending on the constituents to be determined in a given portion. Those with which we shall have to deal are:

1. Fusion with sodium carbonate, for all the main constituents (except ferrous oxide and alkalies), and also for zirconia, baryta, etc.

2. Fusion with calcium carbonate and ammonium chloride, for the alkalies.

3. Fusion with potassium pyrosulphate, for total iron oxides.

4. Solution in a mixture of sulphuric and hydrofluoric acids, for ferrous oxide and for manganous oxide.

5. Solution in a mixture of nitric and hydrofluoric acids, for phosphorus pentoxide.

6. Digestion with hydrochloric acid for sulphur trioxide.

7. Digestion with nitric acid for chlorine.

The reagents employed, and consequently the methods of

[1] Fresenius, 1, pp. 511–521; Hillebrand, pp. 83–90; Mellor, pp. 160–166; Morse, pp. 310–318; Treadwell, pp. 485–491.

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procedure, vary so much that few general rules can be laid down, and the special precautions to be observed in each case will be described in their proper places later. A few general suggestions may be given here.

In a fusion with a powdered flux, such as sodium carbonate, the rock powder and the flux should be well mixed. This may be done with a platinum spatula, and especial care should be taken that the flux is brought well down to the bottom and around all the corners of the crucible, so that no patches of unmixed rock powder are left at the bottom. After smoothing down the surface, the spatula is to be cleaned off by rubbing it on a little flux left on the watch-glass, which is added to that in the crucible.

The mixing of calcium carbonate and ammonium chloride with the rock powder must be so intimate that it demands special precautions, which will be found described on p. 196.

In adding any flux to a rock powder care should be taken that none of the rock powder flies up and is lost.

The heating of the mixture of flux and rock powder should begin very gradually, the crucible at least 10 cm. above a rather low Bunsen flame to drive off moisture. After five or ten minutes it is lowered until the bottom is faintly red; it is kept thus another five to ten minutes, and then the flame is gradually increased until the mass sinters and finally fuses quietly. When the mass is in fusion the height of the flame and of the crucible above it are to be so adjusted that, although the mass is in full fusion, there is no spattering onto the crucible cover, which should be kept on during the whole operation. This will demand some attention at first from time to time, but with practice the right conditions are soon learned. Above all, spattering must not be allowed to take place, even at the expense of greater time for the fusion.

After coming to a state of quiet fusion at a low red heat, the mass should be kept so for at least ten minutes to insure complete decomposition. Blasting is not necessary with most rocks. The liquid will seldom be perfectly clear and transparent, as the carbonates of iron, magnesium and calcium will form cloudy masses within it, so that any such appearances need cause no concern. Indeed, with very femic rocks the mass may seem to be completely fused only around the edges, owing to the abundance of these substances, although the rock is completely decomposed.

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A little sodium carbonate may vaporize and condense on the under side of the cover, but this is of no importance.

The method of loosening the solid cake after fusion is described on p. 136.

In dissolving rock powders in acids, two points are to be specially attended to. The first is the liability of fine powders to fly off when mixed with liquid. This can be avoided by carefully dropping a very little water in so as to moisten the powder, before adding the acid. The tip of the wash-bottle should be full of water so as to cause no puff of air, and it should be inserted beneath the slightly raised crucible cover, which is lowered into place immediately. The second point is that here, also, there should be no spattering, so that the heating should be cautious and gradual at first, and the liquid should never actually boil or bubble.

All evaporations and digestions in which the vapors of strong acids are given off, should be conducted under the hood, which should have an efficient draught. This is necessary, not only on account of the comfort and health of the analyst, but also to prevent contamination of the laboratory atmosphere. Operations that are to be carried out under the hood include: the evaporation of silica to dryness (p. 140) the evaporation of silica with hydrofluoric acid (p. 145) the pyrosulphate fusion of the alumina precipitate (p. 159), the decomposition with sulphuric and hydrofluoric acids for the determination of ferrous oxide (p. 187), and the digestions with sulphuric and hydrofluoric acid for the determination of manganous oxide (p. 221) and with nitric and hydrofluoric acids for that of phosphorus pentoxide (p. 217).

5. Precipitation [1]

The precipitant should be capable of precipitating quantitatively the substance to be determined; should not introduce any substance that may interfere with subsequent precipitations in the same liquid; and any excess of the precipitant should be readily removable from the precipitate by washing.

The ideal precipitate should be insoluble in the liquid in which it is formed; should be wholly precipitated, and as quickly as

[1] Cf. Fresenius, p. 91; Gooch, p. 57; Mellor, p. 95; Morse, p. 198; Ostwald, p. 75; Stieglitz, pp. 122–138, 145–155.

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possible; should not inclose any of the mother liquor, and should not adsorb any of the substances present in the solution; should be in such form as not to pass through the filter, and be readily and completely washed free from impurities; and, finally, should be capable of being changed on drying or ignition to a definite and stable substance of known and invariable composition.

It is seldom, if ever, that we can attain all these optimum desiderata, and we must rest content with reducing the sources of error to a minimum. The following rules will be found generally applicable, but precipitates vary so much in character that some will demand special modifications of treatment.

The solution to be precipitated should seldom be highly concentrated, as the precipitate will then be more apt to adsorb substances present in the solution, and any mother-liquor retained by it will constitute a relatively great impurity. On the other hand, it should not be unduly dilute, partly because no precipitate is absolutely insoluble, partly because more time will be needed for complete precipitation, and partly because it will add to the volume of the liquid to be filtered.

The precipitant is not to be added all at once, but slowly, as this will tend to the formation of, not only a coarser, and more easily washed, precipitate, but one less contaminated with adsorbed substances.

The precipitant should not be added, of course, in such a way as to splash; and if the addition is likely to cause bubbling or effervescence the beaker should be covered with a watch-glass, and the liquid added through a funnel with bent stem.

The solution should be well stirred during the addition of the precipitant, and for a minute or so after, to ensure a thorough mixture. The stirring rod should be so long as to be handled in the subsequent filtration without the fingers coming in contact with the precipitate or the liquid adhering to the rod; it should project about 5–7 cm. above the final bulk of liquid, and, of course, extend above the beaker rim.

A decided, but not extravagant, excess of the precipitant must be added to ensure complete precipitation. This is because of the diminution in solubility of a salt in solution in the presence of an ion common with it.[1] The addition of the exactly theoretical

[1] Cf. J. Walker, Introduction to Physical Chemistry, pp. 329, 351, 1913.

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necessary amount of precipitate never (or almost never) produces complete precipitation, and the excess may be defined as the extra amount needed to bring this about.[1]

No general rule can be laid down as to what this excess should be; but the beginner should avoid adding inordinate amounts of precipitant. To make sure that one has added sufficient, until—and in some cases when—one has had experience, it is well, after allowing the precipitate to settle, to add a few drops or cubic centimeters of the precipitant and observe whether there is further precipitation after a short time. In some cases considerable time must be allowed for this, and then the test may be carried out in the first few cubic centimeters of the filtrate, this being returned to the main portion if a precipitate forms, and more precipitant is to be added to the whole.

Many precipitates are so fine-grained, or even "amorphous," when first formed that they pass through the filter. This is prevented by allowing the precipitate to stand ("digest") for some hours in the solution in which it is formed, before filtration. In this way the larger crystals present grow at the expense of the smaller, and the whole mass of precipitate gradually becomes more coarsely crystalline.[2] Standing in a warm place, as at the back of the steam bath, will facilitate this. Some precipitates, such as magnesium ammonium phosphate, form very slowly, and, with these, standing for some hours, or even a day, is necessary for complete precipitation.

It is often advantageous, as with calcium oxalate, to precipitate in a hot, or even boiling, solution, as this usually has the effect of rendering the precipitate more coarsely crystalline. The solution in which gelatinous substances, as aluminum and ferric hydroxide, are precipitated, should always be hot.

In some cases it is well to add to the solution, before precipitation, a liquid in which the precipitate is but slightly soluble.[3] This not only renders the precipitate coarser-grained, but diminishes the time needed for standing and for complete precipitation. For this reason it is well to add alcohol in the precipitation of calcium and magnesium, and ammonia water as well in that of the latter.

[1] Cf. Gooch, p. 5, Mellor, p. 182, note 6; Ostwald, p. 80.
[2] Cf. Fresenius, p. 92; Gooch, p. 58; Mellor, p. 96; Ostwald, p. 22.
[3] Cf. Fresenius, p. 92; Gooch, p. 58; Ostwald, p. 75.

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Gelatinous precipitates, like aluminum and ferric hydroxides, are not only very difficult to wash free from adsorbed salts, but tend to form colloidal solutions, and pass through the filter. This can be prevented by the presence of electrolytes, such as easily soluble and crystallizable salts, in the solution.[1] Ammonium salts, especially the chloride and nitrate, are generally used for this purpose, as they are driven off on ignition.

Such gelatinous substances should always be precipitated in hot or even boiling liquids. After precipitation the liquid may be brought to boiling, as this effects coagulation. The boiling should not be long continued, as this tends to make the precipitate slimy and difficult to filter and wash. Liquids that contain gelatinous precipitates are very liable to " bump," which may easily lead to loss. They should, on this account, be watched during the heating.

Because of the impurities present in almost all precipitates, and especially in gelatinous ones, through adsorption,[2] co-precipitation, or inclusion of the mother-liquor, which cannot be removed by washing, it is always advisable, if not necessary for good work (when the substance permits), to redissolve the precipitate (after slight washing), and to reprecipitate after a little dilution. If the reprecipitation is effected by neutralization of the acid solution, a small amount of the original precipitant is previously added to ensure the presence of an excess of a common ion.

Before filtration, the precipitate is allowed to stand until the solution above it is clear.

Very small amounts of white precipitates may escape notice. They may be detected by stirring the liquid, when the precipitate collects in a small heap at the center of the bottom of the beaker.

6. Filtration and Washing[3]

The filtration needed in the analysis of rocks is of two kinds: simple filtration, in which a filter paper is used and where the filtrate passes through by its own weight and at practically atmospheric pressure; suction filtration, in which either filter paper or

[1] Cf. Gooch, p. 60; Mellor, p. 95; Ostwald, p. 24; Stieglitz, 1, pp. 125–138.

[2] Cf. Gooch, p. 61; Mellor, p. 96; Ostwald, pp. 18, 84.

[3] Cf. Fresenius, pp. 94–109; Gooch, pp. 62–67; Mellor. pp. 90–106; Morse, pp. 200–208; Ostwald, pp. 13–15; Treadwell, pp. 18–20.

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some other filtering medium, especially asbestos, is used, and the process takes place under diminished pressure, so that the filtrate is " sucked " through the filter. Each method has its advantages, and is specially suited to different precipitates and conditions.

Simple Filtration.—This method is that most generally used, and is the one best adapted to precipitates that can be ignited with the filter paper without change in composition, and specially to cases where the filtrate is to be used for subsequent precipitations.

The funnels and filter papers to be used in this have already been described (pp. 36, 44), and the first requisite is to select the appropriate sizes of filter and funnel. It is a common fault of beginners to use too large a filter, and this is, as Treadwell says: " One of the inexcusable analytical errors."

A filter paper is to be selected that is as small as possible, so as to diminish the amount of washing needed, and yet that will contain all the precipitate and a sufficient amount of wash water; on the other hand, it must not be too small. If the precipitate is very large or bulky it may be advisable or necessary to filter through two filters simultaneously, but this should seldom happen. The size will, of course, differ with the different precipitates, and appropriate sizes are mentioned later in the course of the descriptions of the different methods.

Two principles are, however, to be borne in mind. The first is that " the size of the filter used should be regulated entirely by the amount of the precipitate and not at all by the amount of the liquid to be filtered." (Treadwell, p. 20.)

The second is that, while the filter should be as small as possible, the whole precipitate should not occupy more than one-half, and preferably about one-third of its volume, and should never reach up to less than about 5 mm. of the rim.

The funnel to be used, again, should not be too large for the filter. When folded and put in place the edge of the filter should be about 1, at most not more than 2 cm. below the edge of the funnel. The following sizes will be found appropriate:[1]

Filter	5½	7 . 9	11	12½	cm.
Funnel	3½	4–5	5–6½	6½–7½	7½–9 cm.

[1] Cf. Mellor, p. 90.

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In general, the 9-cm. filter and 6½-cm. funnel are the most used, with the 11, 7, and 5½-filters, and 5 and 3½-funnels, less often needed.

The dry filter is first folded exactly in half, and then again in half (from the center-point of the diameter), so as to form a quadrant. The folds are lightly pressed down with the finger tips, beginning a few millimeters from the tip so as to leave this unpressed, as it might otherwise break or leak. The dry filter is then opened out, placed in the funnel, and fitted snugly into place, which it will immediately do if the apical angle of the funnel is 60°. If this is not exactly 60°, the paper at the second folding is to be folded from the center of the diameter, into slightly more than a quadrant; and is then opened out on the larger or smaller side according as the funnel angle is greater or less than 60°. A funnel had best be rejected for analytical work if its angle is decidedly greater or less than 60°.

Holding the paper in place with a finger tip, the filter is now wet slightly all over with a jet of water from the wash-bottle. Any excess of water is allowed to drain through the stem, and is not poured out, as this may later cause " creeping " of fine precipitates up the glass. With a finger tip the filter is now pressed gently against the glass all over. Care should be taken to press out any air bubbles, and to press down the creases at either side made by the folds, along their length and especially at the rim of the filter, as they are liable to form air channels and retard filtration or lead to loss of precipitate if the filter is, by mischance, overfilled. All this should be done gently and without any rubbing motion, or the tender, moist paper may be torn. If this happens the torn paper is to be rejected and a new one used.

The funnel is then placed in the funnel stand, care being taken that the tip of the stem does not touch the wood in passing. Beneath is placed a beaker of the size suitable to hold the filtrate, as will be suggested in the descriptions of the different determinations. This beaker should be clean, even if the ~~precipitate~~ filtrate is to be rejected, and it is best to rinse it out first with a little water from the wash-bottle. If any precipitate passes through it may thus be recovered unchanged. The tip of the funnel stem should be close to, but not touching, the side of the beaker, and be within about 5 cm. of the bottom, to prevent spattering. As the filtrate accu-

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mulates in the beaker the arm of the funnel stand is to be raised from time to time, so as to keep the tip about the same height above the surface of the liquid.

The beaker with the liquid and precipitate to be filtered, which has been standing until the liquid above is perfectly clear, is held in the right hand [1] above the funnel, the stirring rod (held in the left hand) rested vertically against the lip of the beaker, projecting about 5 cm. below this, and the beaker tilted gently until the liquid flows slowly down the rod [2] and into the filter. The stream is to be directed against the side, not the tip, of the filter, and this should be filled only to within about 2–3 mm. of the rim, so that the edge is kept quite free from precipitate. The liquid should never be allowed to overflow the filter.[3]

If the filter has been properly fitted and the funnel and suction tube are clean, the tube will fill with a column of liquid that causes a gentle suction. Generally, after the column is established the liquid will flow through in a steady stream for the first few minutes. During this time the beaker and rod are to be kept steadily in position above the filter, the tilt of the beaker being gradually increased so as to maintain the level of the liquid in the filter. There must be no "slopping," and as little of the precipitate as possible should enter the filter.

After a time the filtrate begins to pass more slowly and to issue from the stem in drops, because of the clogging of the paper with a little of the precipitate. The beaker may be then, from time to time (to rest the hand), replaced on the bench, and the stirring-rod placed in it, but without disturbing or stirring up the precipitate or resting against the lip. As has been already said, the rod should be long enough to permit handling without touching the adherent precipitate with the fingers. The liquid should be thus poured into the filter from time to time, as it empties, not allowing the filter to empty so far as to break the column in the suction tube.

[1] Here and elsewhere it is assumed that the operator is right-handed.

[2] It is inadvisable to pour the liquid directly from the beaker into the filter without the aid of a rod, as it is apt to drip or splash.

[3] However clear the upper liquid may appear, or however large its volume, it must never be "decanted" directly into the other beaker, but should all be passed through the filter. Particles of precipitate float on the surface or in the mass of liquid and may escape notice, but they would be lost unless caught on the filter.

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If an air-channel develops beneath one of the creases, allowing bubbles to pass into the tube, the open upper ends are to be gently pressed down and closed with the tip of the stirring-rod, without breaking the paper.

As more and more of the liquid passes into the filter the last portion left in the beaker becomes quite thick with the precipitate.[1] If the precipitate is to be redissolved, as will almost always be the case, most of the precipitate should not be allowed to pass into the filter. The sides of the beaker are to be washed down with a little water, directed from the tip of the wash-bottle all around, from the upper level of the adherent precipitate down. After standing a few minutes and allowing the precipitate to settle, the liquid is poured into the filter as before, as little as possible of the precipitate going with it. This washing is repeated only two or three times. The beaker with the precipitate is then substituted for that with the filtrate, the exchange being made so that no drops are lost.

A sufficient amount of the appropriate solvent (generally a dilute acid) is prepared in a small 100 c.c. beaker, and the filter filled nearly to the top with this. As it dissolves the precipitate in the filter and passes through the suction tube [2] it is allowed to drop against the side of the beaker below, above the upper line of adherent precipitate. The beaker is held somewhat slanting and close to the tip of the stem so that the drops do not bounce off. As the solvent drops, the beaker is turned around until all the precipitate covering its interior is acted on and dissolved.

When the filter is empty it is again filled with the solvent, and, if necessary, the solution of adherent precipitate completed, while the stirring-rod is cleaned of precipitate by some drops of solvent running down it. After several repetitions, by which time all the precipitate in the filter should be dissolved, and during which the beaker below is placed upright on the base of the stand and the funnel is lowered to prevent splashing, not more than about 50 c.c. of solvent should have been used.

[1] The description now applies to ordinary, crystalline precipitates. Gelatinous ones need slightly different treatment, as will be described under silica (p. 140), and alumina (p. 152).

[2] A turbidity appearing in the suction tube is but momentary and need cause no concern. It is due to neutralization of the acid by the ammonia remaining in the tube causing reprecipitation.

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The filter is then washed four or five times, the liquid passing of course, into the beaker below, and the sides of the beaker and the stirring-rod are washed down. This should all be done so that not more than 100 or 150 c.c. of liquid and washings containing the dissolved precipitate are in the original beaker.

The liquid is then warmed, a few drops of the precipitant added and reprecipitation brought about by the addition of the proper reagent. During this operation the contents of the beaker are to be stirred constantly. The beaker (covered) is set aside for some time to ensure settling and complete precipitation.

If the precipitate is not to be reprecipitated, the whole loose precipitate, after standing, is brought into the filter with the liquid. The sides of the beaker, from above the line of adherent precipitate, are washed down once or twice and after each washing the contents of the beaker are poured into the filter, which is each time allowed to empty. In what follows the filter is allowed to drain after each addition.

The beaker is then taken in the left hand, held tilted slightly down (mouth to the right) and lip down and above the filter. The rod is placed across the beaker, resting in the lip and the tip projecting a few centimeters, the upper part held firmly in place with the left forefinger. The interior is then washed with a jet of water, commencing on the now upper side, and sweeping the precipitate down. Small portions of water are to be used at a time, and all the loose precipitate is to be washed into the filter.

The beaker being set down, its walls and the rod are well wet with water, and the precipitate adherent to them is rubbed loose with a " policeman " or rubber-tipped rod. This should be done systematically and thoroughly.

The rod is attended to first. Held above the beaker, the portion with adherent precipitate is rubbed along its whole length, the rod being turned so that the whole surface is treated, the tip not being neglected. It is then washed off with a little jet of water into the beaker, and laid across the funnel, after examination to see that it is free from precipitate.

The interior of the beaker is then rubbed clean, also systematically. This may best be done by rubbing a sector of a few centimeters wide at a time, rubbing sidewise from top to bottom;

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then another adjacent sector, and so on. The rubber is occasionally wet with the liquid in the bottom of the beaker. The bottom is finally rubbed clean, best beginning with complete circular sweeps around the bend, and gradually working in to the center. The rubber is washed into the beaker.

All the now loose precipitate is then washed into the filter, as just described. The interior of the beaker is examined in a good light, and any remaining patches of adherent precipitate are rubbed off and washed into the filter, until the beaker and rod are entirely clean and all the precipitate has been brought into the filter.

The whole amount of precipitate should not more than half fill the filter, and should not reach to above 5 mm. of its edge. It is best that the mass of precipitate does not have a flat surface but be rather thicker and lower toward the apex and thinning out of the sides.[1]

Washing of Precipitates.[2]—The precipitate has now to be washed, and in doing this one has to steer between the Scylla of not washing it free from all contaminating salts, and the Charybdis of over-washing and thereby dissolving some of it. It is, therefore most desirable not to wash beyond the point at which the impurities in the wash liquid and adherent to the precipitate are just entirely removed or are reduced to unweighable (and therefore negligible) amount. This will also have the advantage of keeping the bulk of filtrate at a minimum. The theory of the matter is discussed in sufficient detail by the authors cited above so it need not be gone into here.

The general principle to which the discussion leads, and which should be borne in mind and applied in all washings, is that, given a certain amount of liquid, the washing is more efficient, and, therefore, less wash liquid is needed, if it is done with many small portions rather than with a few large portions. In the washing, therefore, the precipitate should be little more than covered with water and allowed to drain each time.

As to the total amount of wash liquid (say water) that should be used no generally applicable rule can be given, as precipitates

[1] Cf. Treadwell, p. 20, Fig. 4.

[2] Fresenius, 1, p. 98; Gooch, p. 62; Mellor, pp. 95–98; Morse, pp. 205–208; Ostwald, pp. 15–22; Treadwell, pp. 18–20.

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vary much in their characters. Theoretically, washing, that is mixing up and rather more than covering the precipitate, four to six times (the filter being emptied each time), should remove soluble salts to such an extent that the residue is negligible. This, however, is seldom actually true, and most precipitates need to be washed (in the sense above) many more times, up to ten or twenty, or more, before the process is complete.

It may be remarked that the tendency of beginners is both to add too large portions at a time, and to overwash, though there are exceptions where impatience leads to underwashing.

In washing precipitates, several practical precautions are to be observed. The jet of water is first directed against the edge of the filter, and carried two or three times around the upper zone that is free from precipitate. This will clear this portion of soluble salts.

The first impact of the jet should never be directed against the precipitate, as otherwise some of the precipitate is liable to be thrown out and lost. It should, therefore, be aimed first at a clean space of the filter and from this gently directed against the edge of the precipitate.

After washing the rim clean, the precipitate is gradually worked downward with the jet, letting the filter empty after it becomes about half full. When all of it has been collected at the bottom of the filter, the mass of precipitate should be well mixed with water several times, great care being taken that none of it is thrown out by too violent an application of the jet, and that not too much water is used. Each time some of the precipitate will be again spread above the main portion, but at the end of the washing the precipitate should be all collected at the bottom of the filter, with the upper part of the sides clean. A little practice will enable one to do this easily.

It is to be remembered that the filter must not be allowed to overflow.

After (not before) the precipitate has been mixed with water three or four times, it will be well to test the filtrate for an impurity, usually chloride or sulphate, that will indicate whether the washing is complete or not. For this, the tip of the suction tube is washed off with a small jet of water, as the previous portions of filtrate are apt to creep up the outside and thus show impurity when the actual liquid in the filter is free from it. A little more

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water is added to the precipitate, the funnel is raised after the column of liquid in the tube has been driven out, and a few drops of the uncontaminated filtrate are caught in a small, clean wash-glass. These are then tested with the appropriate reagent, silver nitrate for chlorides, after the addition of a drop of nitric acid and barium chloride for sulphates. By this time the drops should contain so negligible an amount of dissolved salts that they are to be rejected, even if they show a reaction. This testing is to be repeated after each four or five washings, until there is no reaction. The precipitate is now ready for drying and ignition (p. 101).

Suction Filtration.—This method has the advantage of greatly shortening the time necessary for filtration, but is not well adapted to cases where the filtrate is to be used later. The Gooch modification, however, is especially useful, indeed now almost indispensable, when the precipitate undergoes change on ignition with filter paper, or if it cannot be ignited and must be dried at a low temperature.

The simplest form, in which the filter is of paper and supported in the funnel by a perforated platinum cone, to prevent rupture under pressure, is so seldom used in the analysis of rocks that little need be said of it here.

A funnel with ordinary stem is used, this fitting tightly a single-perforated rubber stopper that closes a filtering flask with stout walls. If it is desired to use the filtrate later, this flask must be well cleaned, but it is better to use Witt's filtering apparatus, with the stem of the funnel projecting into an Erlenmeyer flask.

The perforated platinum cone, best seamless, should fit the funnel accurately. Especial care should be bestowed in fitting the paper closely against both the metal and the glass, which may be done by folding the paper the second time into very slightly (1°–2°) more than a quadrant. If it is not properly fitted it will almost surely be torn at the junction.

The suction should be applied gently and increased gradually, and the final pressure should not be too great; only experience can teach what this should be. The filtration and washing are conducted as in the simple method, except that the funnel may be emptied more frequently, though in the washing the precipitate should be well stirred with water to guard against the formation of channels.

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Gooch Crucible.—In the Gooch method the filter consists of a layer of asbestos supported on the perforated bottom of a crucible, the filtration being aided by rather strong suction. The crucible may be of either platinum or porcelain, but the former is preferable, as it is heated and cooled much more quickly. The appropriate size has been mentioned on p. 31, and the preparation of the asbestos has been described on p. 49. As an example of the usual practice, the filtration of ammonium magnesium phosphate may be taken; that of potassium platinichloride demands some slight modifications in detail, which will be noted in their proper place (p. 205).

The carbon filter tube, inserted in a closely fitting rubber stopper, has a band of soft rubber tubing about 3 cm. long slipped over the wide end, which it should fit closely for about half its length; and the other half, which is bent over horizontally, is cut with scissors, until only a narrow ring of rubber surrounds the interior of the rim.[1]

The stopper is fitted tightly into the filtering flask, and this is connected with the suction. A little of the well-shaken asbestos suspension is poured in—about 2 or 3 c.c., but experience must teach one the right amount. The felt when dry should not be more than about 1 or 2 mm. thick, and may weigh about 5–10 centigrams. The suction is turned on gently and the crucible emptied. It is filled with water five or six times, the jet being directed gently against the side so as not to tear the felt. It is thus washed until no asbestos fibers come through, 50 to 100 c.c. of water being ample,[2] and is finally sucked dry under somewhat increased pressure.

It is sometimes advisable to use a thin, circular, perforated disc, which is placed on a thin layer of wet asbestos first applied and sucked, and the disc covered with an upper layer of asbestos. Otherwise the filter is prepared as above. Though the disc retards the filtration somewhat, it protects the felt and decreases the liability of this being torn. If due care is used, however, I do not find the use of a disc to be necessary.

[1] This is preferable to the arrangement suggested by Morse, p. 202, and Mellor, p. 104.

[2] I do not think that the large volumes recommended by Mellor (p. 105) are either necessary or advisable.

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The crucible is heated over a low flame, the bottom cap being left off, and the flame moved about by hand. In this way the felt is well dried without loosening or blistering, as the steam generated from its lower side will escape through the perforations. When quite dry, as is indicated by the whiteness of the asbestos, the bottom cap is put on, and the crucible is covered and ignited at a bright-red heat for a short time, to drive off all traces of water.[1] It is then cooled in the desiccator and weighed.

The Gooch crucible, with the bottom cap and cover removed, is placed in position in the carbon filter, care being taken when inserting it in the rubber mouth, that the latter does not come in contact with the bottom of the crucible and rub off any small pieces of asbestos which may project beyond the perforations. In order to prevent loosening of the felt by the upward pressure of the air in the flask, the suction should be turned on before inserting the crucible in the filter tube.

The suction should be gentle and at the same time effective. The liquid is poured slowly into the crucible, the stream from the stirring-rod striking the side and not directly on the felt. Otherwise the latter is liable to be torn and some of the perforations laid bare, possibly allowing some of the fine precipitate or asbestos to pass through. The whole of the liquid is thus filtered, with considerable of the precipitate entering the crucible, so as to protect the felt. The beaker is then rinsed with a stream of (in this case) very dilute ammonia water several times, the bulk of the precipitate going into the Gooch crucible. The adhering precipitate is loosened from the sides and bottom of the beaker and from the stirring-rod by means of a rubber-tipped rod, as already described, and the last traces of it brought into the filter by gentle streams of the dilute ammonia from the wash-bottle.

The precipitate on the felt is well washed with the same fluid, the stream being directed against the side of the crucible, not on the felt. The crucible is allowed to empty before each addition, of which about half a dozen will be sufficient in most cases. If desired, the washing can be tested by stopping the suction, removing the stopper of the Erlenmeyer flask, and letting a few drops

[1] If there is no bottom cap, or the crucible be of porcelain, it is placed within another, larger, platinum crucible for ignition.

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fall on a watch-glass. These are acidified with a drop or two of nitric acid and tested with silver nitrate. It will be well to do this the first few times, till one learns by experience when the precipitate is thoroughly washed.

When the washing is complete, the suction is continued for a short time in order to partially dry the precipitate, the connection is shut off, and the stopper is cautiously loosened, so as to prevent regurgitation of any liquid that may remain in the tube, up against the felt. The bottom cap, if there be one, is put on, and the crucible is ready for ignition (p. 105).

7. Drying and Ignition [1]

When the precipitate has been filtered and washed, it has to be dried and brought into a condition of stable and definite composition for weighing. The method to be adopted for this purpose depends on whether or not the precipitate is changed by heating with filter paper or on ignition at a high temperature.

Drying.—When it is a matter of drying at a low temperature such as with the rock powder for hygroscopic water, or potassium platinichloride, the substance, contained in an ordinary platinum or a Gooch crucible, according to circumstance, is dried in the hot-air oven.

Weighed filter papers should never be used, because of the hygroscopicity of paper. The Gooch crucible has entirely supplanted, or at least should entirely supplant them, so that, as Mellor (p. 102) says, their use will soon be obsolete.

The crucible containing the precipitate is covered with a small (7 cm.) filter paper and placed in the oven. The paper prevents contamination by particles falling from the oven top, and at the same time allows the steam to escape. The regular crucible cover is laid aside in a clean place. The door of the oven is closed, the burner underneath is lit, and the temperature is brought gradually to 110°, 130°, or whatever may be required. It is held at this for the requisite time by adjustment of the burner from time to time, if there is no regulator attached. A little practice soon teaches one the right height of flame.

[1] Fresenius, 1, pp. 112–120; Mellor, pp. 168, 183, 213, 219; Treadwell, pp. 21–29.

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The crucible is then placed in the desiccator, its cover is put in place, and it is allowed to cool for weighing.

If the precipitate is collected in a paper filter it should always be ignited from a moist condition. If heating and ignition with paper or carbon changes the precipitate, the Gooch crucible should be used.

The practice, much recommended [1] and frequently used, of drying the precipitate and filter, then removing the greater part of the precipitate, burning the filter paper separately, and igniting the precipitate and ash, is one that, like weighed paper filters, should never be used. The manipulation is very apt, if not almost certain, to lead to the loss of some of the dry powder, and this antiquated method should be superseded by the use of the Gooch crucible.

The ignition of precipitates in a moist paper filter is a simple procedure, and is by far the one most frequently used in the analysis of rocks.

The free edges of the moist filter containing the precipitate in the funnel are loosened and then folded down all around over the precipitate. This is done with the platinum spatula, the end of which should not be soiled by the precipitate. In this way the mass of moist precipitate is completely inclosed in paper.

The funnel being held in the left hand, the little package is gently loosened and lifted by the platinum spatula and is placed in the bottom of a previously weighed platinum crucible. This should, if possible, be not more than half filled by the package. This is laid with the threefold side uppermost, and is pressed snugly down, but without breaking the paper, and leaving a channel on either side for the exit of steam from beneath. The used tip of the spatula is cleaned on a small scrap of filter paper, say one-quarter of a 7-cm. filter. With the same piece of paper, folded once to cover the possible trace of precipitate from the spatula the funnel is rubbed all around at the line of the filter edge to remove any precipitate that may possibly have crept up. The paper, folded up, is placed in the crucible alongside the main mass.

In this way the precipitate may be dried in the crucible without danger of loss from whirling up of powder or from handling of the

[1] Fresenius, 1, p. 510; Treadwell, p. 21.

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crackly and somewhat brittle dried paper that is involved in the earlier method. Incineration of the filter will be complete.

The crucible, with the cover in place, is supported vertically in a triangle and heated above a rather low flame of a Bunsen burner. The appropriate conditions will vary somewhat, but for this stage of the drying the flame should be 5–7 cm. high and the bottom of the crucible 10 or better 15 cm. above its tip. The object is to dry the moist mass of precipitate without boiling of the pasty mass or spattering against the sides of the crucible. One should be patient and heat with great caution to prevent this.

When the mass is dry, and there are no more drops of water on the under side of the cover, the crucible is gently and gradually lowered, a little at a time. When doing this the ring on which the triangle rests should be steadied with the tongs, while the clamp is loosened and the ring lowered.

The paper is carbonized thus very gradually, which is an advantage; as paper carbonized at a low temperature is more easily incinerated than if carbonized rapidly and at a high temperature. The escaping vapors must never be allowed to ignite, as this will very easily cause loss of the powder through the slight explosion at ignition and the currents that are set up. Until the paper is wholly carbonized, as is shown by the pure black color, the bottom of the crucible is not brought close enough to the flame to become red hot.

Ignition.—When the paper is entirely carbonized the crucible is lowered and the flame slightly raised, so that the bottom of the crucible is at a low red heat. The cover is slipped a little to one side so as to allow a little air to enter, the crucible being still vertical, and not on its side at this stage, as is often recommended. The red heat at the bottom is maintained until the paper is wholly burnt away, the flame being somewhat raised toward the last, but never enough to envelop the crucible.[1]

If the carbon of the filter paper or that which penetrates the precipitate burns slowly, its combustion may be hastened by

[1] The flame should not roar, as it so frequently does in unpracticed hands, but the gas and air should be so adjusted that it burns quietly, and without any luminous portion. The adjustment may have to be altered with the raising and lowering of the flame. A roaring Bunsen burner flame, though it sounds like a blast, is no more effective than a quiet one, and is a noisy nuisance to one's neighbors.

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removing the flame and allowing the air to penetrate the cold carbon. On reheating, combustion will usually be rapid. The under side of the crucible cover should always be examined to see if it is free from carbon. If some still adheres after the carbon of the paper is consumed it is burnt off by holding the cover in the platinum-tipped tongs convex side up above the flame for a few minutes.

In general the crucible is then ignited at a bright red heat (about 900° C.), with the crucible vertical, the cover very slightly to one side, and the flame not enveloping the crucible. This ignition may last for thirty minutes, but for many precipitates fifteen to twenty minutes will suffice. The flame is then turned off, the crucible allowed to cool below redness, and, while still warm placed in the desiccator to cool before weighing. Until one has had experience as to the time of ignition, it is well, after weighing, to reheat for ten minutes, cool and again weigh, until there is no loss of weight.

With some precipitates, especially where an oxidizing atmosphere is necessary, as with ferric oxide, the crucible is laid on its side on the triangle, not quite horizontal, the mouth toward one of the ends. The cover is leaned against it with the handle to one side, almost, but not quite, closing it. If the end of the triangle is not twisted, a few notches may be filed along one of the ends to keep the cover from slipping. The flame is applied only to the lower end of the crucible, not near the mouth.

This position of the crucible is much recommended, but, in my opinion, is not well adapted to most precipitates, especially those (such as silica or calcium oxide) which are in the form of light powders, as the danger of loss from draughts is very great. The crucible and cover should never be placed in the quite irrational position sometimes figured.[1] The flame must always play on the base of the crucible, never around its mouth.

The much-used method of drying the precipitate and carbonizing the paper by heating the handle of the cover resting on the vertical crucible is to be discouraged. Besides being unnecessarily tedious, there is great probability of the flame gases entering the crucible and causing the presence of a reducing atmosphere.

In igniting a precipitate in a Gooch crucible the procedure is

[1] Gooch, p. 76; Treadwell, p. 29.

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much the same. If the crucible has a bottom cap, this is put on and the covered crucible heated above a low flame as described above until the felt and precipitate are dry, after which it is ignited at a bright red heat. If there is no cap, the Gooch crucible is placed in a larger platinum crucible and heated and ignited in the same way.

Some precipitates, for example, silica and alumina, require blasting. This is done after the crucible and contents have been heated at bright redness for fifteen minutes. In blasting, the crucible should be vertical, the cover very slightly slipped to one side (about 1 mm.). The flame of the blast should not be large and should be directed only against the bottom and lower third of the crucible.

For many purposes the Meker burner, which gives a hotter flame than the Bunsen, will take the place of a blast. Though it may take slightly longer to dehydrate the substance, there is less liability of loss of weight in the platinum through vaporization if the blast be not used.

If a good grade of filter-paper be used, such as those recommended elsewhere, the weight of filter ash may be neglected in the calculations, as it will fall within the other limits of error. The only general exception would be in the case of the precipitate by ammonia, for alumina, etc., when three or more 11-cm. filters are ignited. The combined weight of their ash may not be negligible in accurate work, and should be deducted from the weight of the ignited precipitate.

8. Titration [1]

In the ordinary course of rock analysis, volumetric operations are made use of only in the determination of the iron oxides, and in the colorimetric methods for titanium manganese, and chromium. They can be used as well for the determination of other constituents, but this is not recommended in rock analysis, where gravimetric methods are preferred for the great majority of

[1] The various text-books frequently cited throughout these pages, especially Fresenius, Gooch, Mellor, Morse, and Treadwell, describe the various procedures of volumetric analysis in more or less detail; they should be consulted by the student for the principles and information that is not given here.

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determinations. No full discussion of volumetric methods, or their principles, will be attempted here, but a few practical suggestions will be made that may be of use to the student.

Volume-Burette.—Two types of burette are in general use, the volume and the weight-burette.

If the volume-burette most often seen is of common Mohr's form, a capacity of 50 c.c., graduated to tenths of 1 c.c., is of an appropriate size. The stopcock should be of glass,[1] and it is best set at an angle of 90°. These burettes should be calibrated, or of the so-called " precision " grade, for good work, and they should be consistent with the measuring flasks used.[2]

The burette should be perfectly dry before the standard solution is introduced, and it is well to rinse it out with a few cubic centimeters of the solution before filling. The standard solution should be taken from the stock bottle with a pipette, not poured out, as this last will disturb its titer. Before taking out any standard solution the bottle containing it is to be gently shaken, so as to wash down any drops of water that may have been deposited by evaporation on the upper walls. The solution is to be introduced into the burette above the zero mark, and allowed to run out until it is level with this. The tip of the burette should be filled in doing this.

The precautions to be observed in reading the position of the meniscus, so as to avoid the effects of parallax, are described by several of the authorities mentioned above. As we have, in rock analysis, to deal only with liquids that are transparent and light-colored,[3] the lower edge of the meniscus is to be used. For reading the position of this, I prefer a general illumination giving the effect shown by Fresenius.[4] The eye must be level with the meniscus, but such devices as floats, striped cards, or a vertical dark stripe at the back, are generally neither necessary nor

[1] Permanganate solutions must never come into contact with rubber, and glass stopcocks are much the best for all purposes.

[2] In the colorimetric methods for which they are used slight discrepancies, say one-tenth of a cubic centimeter, are of no very serious consequence, as the amounts of the constituents determined are small and the consequent errors negligible.

[3] The permanganate solution of proper strength for rock analysis is so light in color that the bottom of the meniscus can be easily seen through it.

[4] Fresenius, 1, p. 46, Fig. 19.

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advisable. One can use a strip of white paper, with a straight edge uppermost, bent around the burette and with the ends of the straight edge meeting. This is moved up or down until the front and rear portions of the straight edge are in line with the lowest point of the meniscus.

In reading a volume-burette a few minutes must be allowed for the drainage of the liquid adhering to the walls above the meniscus, or the reading will be too high. The burette may be gently tapped to facilitate this. For all but the most accurate work there is no need for corrections for temperature.[1]

Weight-burette.[2]—For accurate work the weight-burette has some great advantages over the ordinary form, which make it preferable for use in the determination of the iron oxides. These advantages are:[3] no calibration, is required; no correction for temperature changes is necessary; it is not necessary to wait for drainage; reading the position of a meniscus is not involved; the solution can be weighed readily to 0.01 gram, whereas measurement to 0.01 c.c. is very uncertain.

The burette is provided with a hollow, ground-glass stopper, in which is a small hole, there being a similar hole in the neck. During weighing, the stopper is turned so that the two holes do not coincide, thus closing the burette; before titration the two holes are made to coincide, so that air may enter and the solution escape. The glass protecting cap should be placed on the tip during weighing.

Before use, the burette should be dry, and some cubic centimeters of the solution (permanganate) to be used is shaken in the burette and allowed to run out; this serves to clean it and at the same time saturates the air in the burette with the vapor of the solution. The burette of appropriate size (100 cc. or 50 c.c.) is filled nearly, but not quite to the stopper,[4] this is put into place with the two holes not coinciding, and the protective cap is placed on the tip, great care being taken that the plug of the stopcock is not loosened. The burette is then wiped dry with

[1] A table for these is given by Treadwell, **2**, pp. 534, 535.

[2] M. Ripper, Chem. Zeit., p. 793, 1892.

[3] E. W. Washburn, Jour. Am. Chem. Soc., **30**, p. 40, 1908; R. S. McBride, Bull. Bur. Stand., **8**, p. 617, 1912.

[4] The graduations on the side serve as a guide to the rough measure of the amount of liquid used during the titration; they are not to be used for measuring the exact volume.

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a clean towel, and is weighed. In carrying the burette to the balance case it is well to hold the burette by the neck with the forefinger and thumb of one hand, and with a finger of the other pressing lightly against the cap, so that this may not slip off and be broken. The burette may be handled with dry fingers. In weighing, it is suspended by a loop of wire attached to it from the hook above the left-hand pan. After weighing it is placed in the clamp with rubber-covered jaws, which are gently screwed up so as to hold the burette in place, but without danger of crushing it.

The Operation.—To allow the liquid to escape, in working with either form of burette, the cock is best managed with the left hand, the right being used to rotate or stir the liquid in the iron titration. The sides of the plug and of the socket should be straight and strictly conical and well-fitting, so that they do not jam on turning. In turning the cock, care should be taken, on the one hand not to bear down so heavily as to cause the plug to stick in the socket, and on the other not to raise the plug so as to let liquid escape between the plug and socket. The tip should not be so high above the liquid below as to cause splashing of drops.

The liquid must be added cautiously, and after each addition, the flask is rotated or the liquid stirred. Toward the end, the addition must be drop by drop, great caution being needed not to overrun the end-point. When the total amount is known approximately, then the first additions of the standard solution may be relatively large but the end-point must be approached with the same degree of caution.

The end-point, as in iron titrations, is partly a matter of judgment as to what shade of color is to be taken as representing it. In iron titrations the first pink blush, that remains permanent after a minute's stirring or rotation, is to be taken; but this should correspond with that which has been selected in the standardization of the permanganate solution. A single drop should be sufficient to cause the change, though in the titration for ferrous oxide the decision as to the end-point is complicated by the presence of hydrofluoric acid, which renders the color evanescent, as we shall see.

More details will be found in the descriptions of the various methods in which a burette is used, those for ferric and ferrous oxides, and the colorimetric methods for titanium and manganese.

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PART V

METHODS

1. General Course of Analysis

Before beginning the detailed descriptions of the methods for determining [1] the various constituents, it will be advisable to state concisely what the course of analysis is, in what separate portions the different constituents are determined, and the plan of separation, in order to obtain a general survey of the analysis, so that the details may be considered later with greater intelligence and knowledge of their relations to the whole analysis. In this summary, if there are several alternative methods which are described subsequently, only that one will be mentioned which especially recommends itself for the use of students, and which, in general, I have adopted for my own work.

a. Silica, alumina, total iron oxides, titanium dioxide, lime, strontia, and magnesia, are determined in a portion of 1 gram, which is usually called the " main " portion. The powder is fused with five times its weight of sodium carbonate, and the cold cake is dissolved in hydrochloric acid and the solution evaporated to dryness, thus rendering the silica insoluble. The silica is filtered off and in the filtrate, alumina, ferric oxide, titanium dioxide and phosphorus pentoxide are precipitated by ammonia water, with or without the addition of ammonium persulphate. After filtration the precipitate is dissolved in nitric acid and reprecipitated by ammonia, and this is repeated if there is much magnesia present. The precipitate is ignited and weighed, and then brought into solution by fusion with potassium pyrosulphate. The melt is

[1] The phrase " to determine " is more appropriate than " to estimate"; the former is defined as " to ascertain definitely," and the latter as " to form a judgment regarding the value, etc., of." The former is definite, the latter is approximate. Compare Mellor, p. 672.

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dissolved in water, the ferric oxide is reduced by hydrogen sulphide, the excess of this boiled off, and the total iron oxide is determined by titration with potassium permanganate. Titanium dioxide is determined in the same liquid by the colorimetric method, which consists in comparing the intensity of color of a known volume of the liquid after oxidation by hydrogen peroxide, with that of a standard solution of titanium colored in the same way.

The filtrate from the ammonia precipitate is precipitated with ammonium oxalate, the precipitate of calcium oxalate dissolved and reprecipitated, and the lime determined as such by ignition of the oxalate.

Strontia may be determined in the weighed lime, obtained as above, by solution in nitric acid, evaporation to dryness, solution of the calcium nitrate by a mixture of ether and absolute alcohol, solution of the strontium nitrate in water and precipitation of the strontium as sulphate after addition of alcohol.

In the filtrate from the calcium oxalate the magnesia is determined by precipitation as ammonium-magnesium phosphate, which, after solution and reprecipitation, is ignited. The magnesia is weighed as pyrophosphate. The filtrate from this last operation is rejected.

b. Ferrous oxide is determined in a portion of powder of half a gram by solution in a boiling mixture of hydrofluoric and sulphuric acids, the operation being conducted in a well-closed platinum crucible. The contents of the crucible are transferred to water and titrated with potassium permanganate.

(*c*) Alkalies are determined in a portion of half a gram of specially ground powder which is effected by the Lawrence Smith method. The powder is intimately mixed with ammonium chloride and calcium carbonate, and heated under the proper conditions. After thorough leaching, the filtrate is precipitated with ammonium carbonate, and the filtrate from this is evaporated to dryness. The ammonium chloride is driven off by cautious heating, and the chlorides of sodium and potassium are weighed. The potassium is separated by chloroplatinic acid, and is weighed as platinichloride, the soda being determined from the weight of the mixed chlorides by difference.

(*d*) Combined water is determined by Penfield's method in a portion of $\frac{1}{2}$ to 1 gram. The powder is ignited in a dry glass tube

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sealed at one end, and the water driven to the cool portion of the tube; the end containing the powder is drawn off, and the water weighed in the remaining portion. The amount of hygroscopic water is deducted.

(*e*) Hygroscopic water is determined in a portion of about 1 gram by heating at a temperature of 110°. This portion is to be used afterward for the determination of other constituents, as P_2O_5, MnO, or S, ZrO_2, and BaO.

(*f*) Phosphorus pentoxide is determined by digestion of a portion of about 1 gram with nitric and hydrofluoric acids, removal of silica by evaporation, and subsequent precipitation as ammonium phosphomolybdate. This precipitate is dissolved in ammonia water, the phosphorus is thrown down by magnesia mixture as ammonium magnesium phosphate and weighed as magnesium pyrophosphate.

(*g*) Manganous oxide is determined in a portion of 1 gram, the rock powder being broken up by heating with sulphuric and hydrofluoric acids, the latter being driven off. To the filtrate a solution of silver nitrate and some ammonium persulphate are added and the liquid heated, the manganous salt being oxidized to permanganate. The manganese in this solution is then determined colorimetrically, by comparison with a standard solution of manganous sulphate similarly treated.

(*h*) Total sulphur, zirconia, the rare earths, and baryta may be determined in a portion of 1 gram. The rock powder is fused with sodium carbonate, and the melt leached with water. After acidification of the filtrate with hydrochloric acid, the sulphur is precipitated and weighed as barium sulphate. The zirconia is dissolved out of the residue insoluble in water by very dilute sulphuric acid, and, after addition of hydrogen peroxide, is thrown down and weighed as basic phosphate by the addition of sodium phosphate. In the filtrate from this precipitate the rare earths may be determined. The barium remains as sulphate after solution of the zirconia. It is brought into solution by fusion with sodium carbonate, which converts it into carbonate, the melt leached with hot water, and the residue dissolved in hydrochloric acid. It is precipitated as sulphate, in which form it is weighed.

(*i*) Sulphur trioxide is determined in a portion of about 1 gram

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by digestion with dilute hydrochloric acid and precipitation as barium sulphate.

(*j*) For chlorine a portion of 1 gram is digested with chlorine-free nitric acid, and the chlorine precipitated in the filtrate by silver nitrate.

(*k*) Fluorine is determined in a portion of 2 grams by fusion with sodium carbonate, leaching with water, and precipitation of the filtrate with ammonium carbonate, the filtrate from which is precipitated with an ammoniacal solution of zinc oxide. In the filtrate from this a mixture of calcium carbonate and fluoride is precipitated by calcium chloride, and the calcium carbonate dissolved out by acetic acid, leaving the calcium fluoride, in which form the fluorine is weighed.

(*l*) A portion of from 2 to 5 grams is used for the determination of carbon dioxide. The rock powder is decomposed by hydrochloric acid in a small flask, and the carbon dioxide is absorbed in a weighed U-tube containing soda-lime, precautions being taken to keep the apparatus full of a current of air free from carbon dioxide, and to properly dry and purify the gas given off from the rock.

(*m*) For chromium sesquioxide a gram of rock powder will suffice, though 2 grams are preferable. After fusion with alkali carbonate and a little potassium nitrate, and subsequent leaching with water, the chromium is determined as chromate in the filtrate by a colorimetric comparison of a known volume of the solution with a standard solution of potassium chromate. If necessary, the solution is concentrated by evaporation before making the comparison.

In regard to the weight of the portions which it is recommended to take for the various determinations, it should be borne in mind that they are intended for the great majority of rocks, but that in exceptional cases they are to be departed from according to the judgment of the analyst. For instance, in the analysis of iron ores, if a gram be taken for the main portion the bulk of the voluminous precipitate of ferric hydroxide will be so great that it cannot all be brought on one filter, and possibly not on two. Of such rocks, therefore, only half a gram of powder need be taken, even though extra care must be paid to the determination of other constituents. On the other hand, for the

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determination of alkalies in peridotites and other rocks in which their amount is extremely small, a gram or two of powder should be taken, instead of the half gram which is usually sufficient.

The criticism is sometimes made that portions of 1 gram or of ½ gram are so small that they are inadequate to yield on analysis a just idea of the actual proportions of the several constituents in a mass of rock. It is, of course, generally true that the larger the amount of substance, within limits, that is taken for analysis the greater will be the accuracy; that is, the more negligible will be the errors incident to the various operations in comparison with the mass taken.[1]

Considerations of practicality, however, such as the amount of material available, the practically manageable sizes of utensils, and, above all, the time involved in the different operations, set limits on the amount of the portion to be taken. Morse points out also the consideration that the use of large quantities permits of (and therefore tends to encourage) careless methods of work without seemingly impairing the accuracy of the results.

We must compromise between the theoretical advantage of greater, and the practical advantages of smaller, weight of substance taken. Long experience of analysts has clearly taught us what are the optimum amounts to be taken in particular cases, and the student should adhere to these whenever possible; it being assumed that the specimen of rock powder has been properly sampled and so the whole, and consequently a portion of it, is representative of the rock mass.

2. Time Needed for an Analysis

In answer to the question "How long does it take to make a complete rock analysis?" Hillebrand[2] states that, given ample and adequate laboratory facilities and apparatus, it is possible for an experienced and quick worker to complete an analysis of a series every three days, after the first is finished, barring delays. While this is possible, the analyst is not generally dealing with a series of analyses, but is more concerned about the time needed for the completion of a single one.

[1] Cf. Morse, p. 214; Fresenius, **1**, p. 71.
[2] Hillebrand, p. 30.

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The time necessary for performing the separate parts of the various analytical operations are more or less fixed at minima by the conditions and circumstances of each. The times, however, may often be very largely controlled by the skill and judgment of the analyst. Thus, although the calcium oxalate precipitate must stand for a given number of hours, the careful and experienced analyst will take much less time than the beginner in its filtration, and will use much less water in washing it, and so lessen the time needed for the magnesia determination. Again, the skillful analyst will carry out two or three filtrations simultaneously, while other operations are proceeding automatically; the beginner will find his time fully occupied with one filtration, and will probably have forgotten to utilize the time for automatic parts of other operations.

The beginner in analytical work has a strong tendency to use too large vessels and filters and to overwash precipitates; both of which lead to unnecessarily large amounts of filtrates. He also is very apt to ignite precipitates for an inordinate length of time. All such practices, which are mostly due to conscientious excess of care, not only increase the time needed for analysis, and in the aggregate greatly so, but make for lessening rather than for increasing the accuracy of the work.

The beginner is also very apt to leave a slow-running filtration "for a minute," forget it in the interest of some other process, and thus lose time or get into difficulties, for example, with gelatinous precipitates.

Besides the general fundamentals of care, cleanliness, and conscientiousness, there are two short maxims that it will be well for the beginner to bear constantly in mind and conform to, if he wishes to complete an analysis in a reasonably short time. These are: "Be always on the job" and "Keep the sizes and volumes small."

The analyst should not be content to wait for each partial operation to be terminated before beginning another, but should avail himself of the opportunities which present themselves for carrying on simultaneously as many separate operations as it is possible to do with success. The ability to do this naturally grows with experience in the purely mechanical execution, and also with judgment as to the best way of economizing time. It is not recommended that the novice should attempt very much in this way,

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and he will probably find that two or three operations at once are all that he can cope with successfully at the start. But he should constantly bear in mind the manifold possibilities in this direction, and, with growing experience, avail himself of the various opportunities that present themselves.

With some practice, the number of different operations, both active and passive, which may be conducted simultaneously or nearly so, may easily reach six or more. Thus during the filtration of the first precipitate of ammonium magnesium phosphate, the following operations may be carried out: The evaporation of the solution of the alkali chlorides, the expulsion of H_2S, from the reduced iron solution, and the ignition of the precipitate of calcium oxalate. As a matter of fact, the precipitates by which phosphorous pentoxide, sulphur, baryta and zirconia are determined may be ready for filtration about the same time as the ammonium magnesium phosphate and the filtration of about two of these precipitates may be carried out with the latter. Any such combination implies, of course, a sufficiently liberal supply of apparatus so as not to be kept waiting for lack of the necessary utensils, and it also assumes that the analyst may devote several hours continuously at a time to the analysis.

To come to concrete figures,[1] it is easily possible to finish an analysis involving the determination of eighteen or twenty constituents in five days, not necessarily consecutive, of eight or nine hours each without interruptions, and even in less time. Such an analysis can surely be made in six days without any special effort at economizing time. Indeed, a comparatively simple analysis, in which a dozen constituents are to be determined, may be completed readily in four days without any sacrifice of accuracy, but this last is possible only in the hands of a quick and experienced worker with proper facilities.

In the present section some suggestions are made of the possibilities in the way of economizing the time of analysis.[2] They are not intended to be final, but will serve merely as guides in laying out the plan of analytical work, and are subject to modification to suit the exigencies of each particular case. In connection

[1] Hillebrand, p. 30.

[2] These suggestions are based on an analysis made especially for this purpose, the results of which are given on pp. 243–246.

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with them some estimates are given of the time which is needed for the several operations and determinations. These, again, must be regarded as only rough approximations, which will vary with different laboratory facilities and with the skill and experience of the operator. They will have to be extended somewhat when the analysis is conducted by a novice.

Assuming that we start Monday morning at nine o'clock, with about 50 grams of rock chips, these can be reduced to powder ready for analysis in less than an hour. Weighing out the crucible and the main portion (p. 129) will take about fifteen minutes. The main fusion with sodium carbonate (p. 131) is then begun at about ten o'clock, the time needed for the fusion and cooling being about one hour. During this time another separate portion can be weighed out, dried for half an hour at 110° for the hydroscopic water, and the portion mixed with sulphuric and hydrofluoric acids and started evaporating for the determination of manganous oxide (p. 219).

When the carbonate cake is cold it is transferred to the platinum basin. About one hour will be consumed in bringing this cake into solution. The evaporation of this liquid to dryness to render the silica insoluble will take until nearly three o'clock. During this time the determination of alkalies can be begun (p. 191). The special grinding and weighing out of the powder, and mixing with calcium carbonate and ammonium chloride, will take one-half to three-quarters of an hour, and the subsequent ignition another three-quarters of an hour, during which a portion can be weighed out for phosphorus pentoxide and its evaporation with nitric and hydrofluoric acids be begun (p. 216).

One should have time toward the end of the afternoon to wash the silica and begin the evaporation of the filtrate for the recovery of the extra trace of silica. This second evaporation may be continued until the close of the day (it will take about one hour and a half), or it may be continued on the steam bath over night. If that is not available it can be finished the first thing next morning. It will be seen that the first day is mainly one of decompositions and preparation.

On Tuesday morning the silica is first attended to. The washing of the recovered silica, and the ignition and burning off of the small filter will not take more than half an hour, after which the

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heating and ignition of the silica will begin, which will take an hour and a half to two hours.

During the ignition of the silica, the precipitation and filtration of the ammonia precipitate (p. 146) can be begun. If three precipitations are necessary this will take nearly three hours, and will demand almost constant attention. During this time, however, the ignited silica can be weighed and its evaporation with hydrofluoric acid started, the evaporation taking nearly an hour. This can be finished by the time the final ammonia precipitate is ready to put in the crucible with the residue from the silica and its heating is begun. It may be possible to get this alumina precipitate dried and ignited by the end of the day, if it is not large.

When the filtrations from the alumina precipitate are finished they are brought to a boil and the lime is precipitated with ammonium oxalate (p. 177). It is better, and involves no real loss of time, to let the beakers with the calcium oxalate precipitates stand over night.

Time should be found this afternoon (Tuesday) to leach the cake from the alkali fusion, which has been soaking in a little water in the crucible over night, and also to precipitate the trace of lime in the solution with ammonium carbonate and filter off the precipitate. The evaporation of the filtrate containing the alkali chlorides can be begun and at least partly finished this day.

On Wednesday, the fusion of the alumina precipitate in pyrosulphate (p. 159) will be completed. The time needed for this is uncertain, being largely dependent on the amount of iron oxide present, but it will often be possible to reduce and determine the total iron oxides on the same day that the fusion with pyrosulphate is begun. The alkalies can also be finished during this day.

The calcium oxalate precipitate is filtered off, redissolved and reprecipitated in the morning, and the lime weighed after the precipitate has stood for two hours or so. Sodium ammonium phosphate is added to the filtrate to precipitate magnesia (p. 180), and the beakers are allowed to stand over night.

On Thursday, the magnesia precipitate can first be filtered off, redissolved and reprecipitated. It can be filtered off, ignited and weighed late in the afternoon, or this can be done Friday morning. The alkalies are to be entirely finished this day, if they have not been done before, as should have been easily possible. The evap-

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oration to dryness of the alkali chlorides will take an hour to two hours on the water-bath; their weighing, fifteen minutes, and the evaporation of the platinichloride solution should not take more than half an hour. The filtration in a Gooch crucible and the drying and weighing of the potassium platinichloride ought to be completed in about an hour. The actual time actively spent in these operations is small.

The total iron oxides (p. 162) can be titrated this morning, if this has not yet been done. The time needed for reducing the ferric to ferrous oxide with hydrogen sulphide will vary from one-half to three-quarters of an hour, the filtration of this solution may take another half hour, the expulsion of the hydrogen sulphide by boiling and the subsequent cooling of the liquid should be over in less than an hour, while the actual titration should be done in about twenty minutes, including the weighing of the burette twice.

When the total iron oxides have been determined the colorimetric determination of titanium dioxide (p. 167) can be carried out. All of this operation should not take more than one one-half or, at most, three-quarters of an hour.

The determination of ferrous oxide should also be done on this day, though time might have been found for it before, as the operation should not take more than about one-half an hour, during which, however, it will need constant and undivided attention.

It should also be possible to complete the manganese and phosphorus determinations this day, and sulphur and baryta or zirconia, if these have been begun previously. Time can also be found for making the total water determination, an operation that will consume little more than half an hour.

The whole analysis should, therefore, be completed by Thursday evening, but, if not, Friday morning should see the completion of the various end determinations, such as the magnesia, manganese, phosphorus, zirconia, etc.

It will be found that there will be many intervals during which parts of the determinations of the minor constituents can be carried out, as these call for small volumes of liquid and so can be readily done in the gaps between the parts of the major operations.

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3. Errors and Summation

Character of Errors.—It is well recognized that no analysis can be ideally perfect; that is, yield results that show the proportions of the various constituents with absolute accuracy. No analyst is continuously, to say nothing of wholly, perfect in his manipulations; no piece of apparatus is entirely free from faults and no reagent free from all impurities; no conditions can be completely controlled; lastly, no method for any determination is known that has not inherent in it some source or sources of error. The best that the analyst can do is to strive to reduce to a minimum the various errors that may arise.

In connection with the descriptions of the various methods for the determination of the several constituents there will be discussed the particular errors inherent in each. It will be well, however, to present to the student some ideas on the general characters of analytical errors, so that he may deal more understandingly with the particular cases as they arise.

Analytical errors may be referred to two broad groups, which may be called the "operative" errors or errors of operation, which are incident to an operation or to the manipulation, and the "methodic" errors or errors of method, which are inherent and peculiar to the various methods.[1]

The "operative" errors are those such as are caused by the entrance of dust, spilling of drops and other mechanical losses, or too long-continued washing of precipitates.[2] The "methodic" errors include such as those due to co-precipitation of magnesia with alumina, the ready oxidizability of ferrous compounds, or the strong adsorption of salts by gelatinous precipitates.

These differ essentially in that the operative errors are due to causes outside the chemical and physico-chemical factors of the analysis; while the methodic errors are dependent on the chem-

[1] This division is one of practicality and differs from the usual division into "accidental" and "systematic" errors, which are especially adapted to mathematical treatment. See Mellor, Higher Mathematics for Students of Chemistry, 1905, pp. 502, 529.

[2] Included among them are also "personal" errors and those due to impurities in reagents, inaccuracy in instruments, and the non-determination of constituents. Operative errors are discussed on pp. 75–79.

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ical characters and peculiarities of the substances involved and on the conditions under which they are made to react.

That the one group may grade into the other, so to speak, is shown by such examples as the errors due to the overwashing of precipitates and to the adsorption of salts, in which it is a case of attaining correct results by the balancing of operative manipulation against peculiarities inherent in the method.

The occurrence of operative errors is brought about mostly by carelessness in manipulation, so that they are, or should be, almost entirely avoidable, they should be always eliminated so far as possible by the use of skill, dexterity, cleanliness, and thought.

The methodic errors, on the other hand, are inherent in the particular methods, and so can seldom, if ever, be wholly eliminated. They can, however, be controlled and reduced to a minimum by sufficient knowledge and consequent attention to the proper conditions of reaction.

Some of the operative errors, such as the entrance of dust or the spilling of drops, are so obvious that nothing need be said of them to the intelligent and conscientious student. Others have been briefly dealt with in the section on operations, and some precautions have been pointed out by which they may be avoided. In the subsequent part of this book, in general, the operative errors will be assumed to be known and guarded against, and only those of a methodic character will be considered and discussed.

Direction of Errors.—The characters of the probable systematic errors to which the determinations of the several more important constituents are subject will be discussed in connection with the descriptions of the various methods. It may be of interest and use to the student to summarize very briefly the probable direction of methodic error [1] of the more important constituents, whether plus or minus; that is, whether, because of them, a careful worker may be prepared to expect a result to be higher or lower than the truth.

Dittrich [2] has investigated this subject as regards alumina, ferric oxide, lime, magnesia, soda, and potash. Some of his

[1] It is understood that such operative errors as those due to spilling of drops, overwashing of precipitates, entrance of dust, impurities in reagents, and many others, will not be considered here.

[2] M. Dittrich, Neu. Jahrb., 2, p. 69, 1903.

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methods were poor and one-half of the analyses were carried out by incompetent assistants, so that his results are of little value. Robinson [1] has tabulated the probable direction of error for the more important constituents, basing his conclusions on many analyses made by several analysts according to the methods given by Hillebrand. Some very instructive comments on a large series of analyses of samples of the same argillaceous limestone are given by the Committee on Uniformity in Technical Analysis.[2]

The general conclusions to which I have been led,[3] independently of this report, by consideration of the methods employed and from critical study of very many analyses of igneous rocks are as follows:

Silica.—The errors incident to this determination are, on the whole, of small magnitude and with a tendency to the minus side. If a second evaporation for silica is made, and that which is dissolved in pyrosulphate is recovered, they may be regarded as negligible; the more so as silica is, in the vast majority of rocks, the constituent that is present in the largest amount, and its determination does not affect that of others. In judging analyses of inferior quality I have found that the determination of silica (with that of lime) is the one in which most confidence can be placed.

Alumina.—This constituent is more subject to error, both in magnitude and variety, than any other of those determined in all rock analyses. These errors may be of very serious consequence, despite alumina being usually the most abundant constituent (next to silica), as its correct determination is of great importance in many mineralogical calculations.

The errors for alumina in the aggregate tend to be plus; though there are a few minus ones, these are generally much more than outweighed by those that are plus. This plus tendency is increased in incomplete analyses by the indirect determination of alumina by difference, so that the neglect of any of the constituents that are weighed with it will increase its apparent amount.

In the hands of incompetent or inexpert workers, the two chief sources, non-determination of constituents that are weighed with

[1] H. H. Robinson, Am. Jour. Sci., **41**, p. 259, 1916.
[2] Jour. Am. Chem. Soc., **28**, p. 232, 1906.
[3] Washington, Prof. Paper 99, pp. 13, 20.

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alumina (p. 8) and the co-precipitation of magnesia, as well as the difficulty of washing the precipitate, with the determination of alumina by difference, cause the figure for alumina to be almost invariably and inevitably high—often by several or many per cent. Even in the hands of careful workers, though alumina can be determined with almost as much accuracy as can most of the other constituents, there is a liability to variation or irregularity, with a plus tendency.

The determination of alumina must be regarded as the most unsatisfactory of all, even for the expert analyst, and, because of its importance, an accurate method for its direct determination is the most urgent need in the analysis of rocks.

Ferric Oxide.—Failure to reduce the ferric oxide completely to ferrous and loss through " creeping " in the pyrosulphate fusion tend to minus errors, while reduction with zinc and deterioration of the permanganate solution have the opposite effect. These main sources of error, however, should not be of great magnitude if the work is carefully done. In general, I think that the tendency with ferric oxide is toward minus, rather than plus error, and that it is seldom serious with a careful worker. If zinc has been used for the reduction it is almost certainly plus.

Ferrous Oxide.—This has always been, and probably will remain, the direct determination in rock analysis that is most fraught with uncertainty and difficulty in obtaining very accurate results. These arise, for the most part, from the ready oxidizability of the constituent and the difficulty in bringing it, unoxidized, into solution from the not easily soluble or decomposable silicates. This liability to oxidation and difficulty of decomposition tend, of course, towards low results. The only important factors of opposite tendency are the evanescent and uncertain end-point produced by hydrofluoric acid and the influence of manganous oxide in the permanganate titration. The plus tendency caused by organic matter, sulphides, and vanadium may be disregarded with most rocks. On the whole, there is a strong tendency to minus error in the determination of ferrous oxide.

Lime.—If the ammonia water is free from carbonate and the calcium oxalate is dissolved and reprecipitated, there are no serious systematic errors in the determination of lime. Indeed, the figures for lime, as well as silica, can generally be taken with confidence

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as to their approximate accuracy, even in otherwise rather poor work. The error may be considered as having a very slight plus tendency, so small as to be negligible.

Magnesia.—Unless the analytical work is very careless, there should be little serious error in the determination of magnesia. The liability to precipitation of an ammonium magnesium phosphate of abnormal and variable composition, which tends to plus errors, is readily eliminated by solution and reprecipitation under proper conditions. The retention of magnesia with the alumina, due to paucity of ammonium salt, is possible or probable with ignorant, careless, or hasty work, of which, indeed, it may be considered to be one of the characteristics. This minus error may be of very serious magnitude. With good analysts the error in magnesia may be considered as plus or minus, that is, probably negligible; while with inferior workers it is almost always minus, and often very highly so.

Potash.—With both potash and soda, if the Smith method of decomposition is used (as is assumed), there is some tendency to minus error, because of retention of alkali chloride in the fusion cake through incomplete leaching. This should, however, be very small. The plus error due to alkali in the calcium carbonate is easily eliminated by making the proper correction, as should always be done if the carbonate is of such poor quality as to call for it. Errors due to other causes are so small in good work as to be negligible. On the whole the error tendency in potash may be regarded as negligible, but with a slight leaning toward minus.

Soda.—The remarks just made in connection with potash, as to the errors due to incomplete washing and to alkali in the carbonate, apply equally well to soda. As the amount of soda is generally greater than that of potash, and as it is determined by difference, these errors may be somewhat magnified with soda. The general tendency is the same as with potash. In my experience I have found both the alkalies to be among the most accurately and consistently determinable of the rock constituents.

Water.—Unless the rock is high in ferrous oxide and the water is determined "on ignition," there are no notable errors in the determination of water, either "combined" or "hygroscopic." The amounts are usually so small, and this constituent is as a rule so unimportant, that the errors may be regarded as insignificant.

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Titanium Dioxide.—If the colorimetric method is used, the errors in this determination are small and, because of the generally small amount present, are seldom serious. Because of the bleaching effects of hydrofluoric acid and alkali sulphates, as has been pointed out by Merwin, there is a tendency toward small minus error. If the antiquated methods based on boiling acid solutions be used the errors are variable in direction and may be relatively large; they are probably generally plus.

Phosphorus Pentoxide.—The errors incident to the determination of this are so seldom serious, and the usual amounts of this constituent are in most rocks so small, that they may be considered as insignificant. The tendency, if any, is toward very slight plus error.

Manganous Oxide.—If the colorimetric method is used the errors in the determination of manganese are negligible, particularly as the amount present is almost always very small. If the basic acetate method is used and the analyst is not expert, there is a decided tendency to plus error, which may be of both relatively and absolutely large magnitude.[1]

In the determination of the other minor constituents the possible errors, though sometimes relatively great, are usually of such slight absolute importance that their directions need not be considered. As Hillebrand remarks of the rarer constituents: "It is often more important to know whether or not an element is present than to be able to say that it is there in amount of exactly 0.02 or 0.06 per cent."

Limit of Error.[2]—Inasmuch as no determination can be expected to yield perfectly accurate results, or to be exactly reproducible on duplicate analysis, except by chance, we must assume some limits for the possible variation on either side of the truth, such that values falling within them may be regarded as satisfactory and consistent with good work. These limits may be called "allowable."

In attempting to allot the allowable limit of error for each constituent, regard must be had to its amount in any given case. Assuming that the allowable total error is ± 0.60, which is not

[1] Cf. Hillebrand *et al.*, Jour. Am. Chem. Soc., **28**, p. 233, 1906.

[2] Cf. Hillebrand, p. 27; Mellor, p. 247; Dittrich, Neues Jahrbuch, **2**, p. 69, 1903; Hillebrand *et al.*, Jour Am. Chem. Soc., **28**, pp. 223 ff, 1906.

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quite correct, but near enough for the present purpose, we might allot this proportionately among the chief constituents somewhat as follows: Taking, for example, the average igneous rocks as calculated by Clarke[1] we would obtain these figures: SiO_2 ± 0.35, Al_2O_3, ± 0.10, Fe_2O_3 ± 0.02, FeO, MgO, CaO and Na_2O ± 0.03, K_2O ± 0.02, H_2O, TiO_2, P_2O_5 and Mno ± 0.01. These are based on the assumptions that the errors may be all in one direction and are proportional to the amount of each constituent.

We cannot, however, always expect such close agreement in duplicate determinations of the less abundant constituents as is implied by these figures. The matter is further complicated by the varied differences in difficulty and possible exactness that condition the several determinations, particularly as some of the errors may probably compensate for each other to some extent.

Without going into a full discussion of this subject, and disregarding the various details that are peculiar to the several constituents, we may provisionally assume the figures given below as the allowable limits of error for constituents that are present in about the amounts mentioned.

It will be understood that the limits mentioned are in percentages of the whole rock, not of the amount of each constituent.

These allowable limits are: for SiO_2 and others that amount to 30 per cent or over, from ± 0.10 to ± 0.15; for Al_2O_3 and others that amount to from 10 to 30 per cent, ± 0.05 to ± 0.10; for constituents that amount to from 1 to 10 per cent, ± 0.03 to ± 0.05.

These figures are but approximate suggestions, based on experience in analysis and in the critical judging of analyses. They mean that duplicate determinations should not differ from each other by more than these amounts, while it is very desirable, and usually quite possible in good work, that they fall well within them.[2]

The difference may, under peculiar conditions or with particular rocks or minerals, and with certain methods, be somewhat greater than those mentioned, without reflecting seriously or at

[1] F. W. Clarke, U. S. Geol. Surv., Bull. 616, p. 27, 1916.

[2] The student will find many such examples among the mineral analyses of Penfield and many others in the 3d and 4th series of the American Journal of Science; and some of rock analyses in U. S. Geol. Survey, Prof. Paper 99. An excellent example, with comments on other work on the same material, is that on p. 229, Jour. Am. Chem. Soc., **28**, 1906.

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all on the quality of the analysis; but such cases are to be judged only by the experienced analyst. The student should not think that the somewhat liberal latitude here given in these allowable limits of error justifies him in taking advantage of them as an excuse for poor work. He should, on the contrary, endeavor to make his analyses so that the differences between duplicate determinations, if they are made, fall well within the limits thus allowed.

In order to check his errors, and so be in a position to correct them, the novice should make duplicate analyses throughout, until he becomes familiar with the methods and the manipulations, and by repeated close agreements may place justifiable confidence in his single determinations. This will, at first, involve more labor and the turning out of fewer analyses in a given time; but the increased value of the results will much more than compensate for this in the end. An analysis in which the analyst himself cannot place implicit confidence is not only of little use, but is positively dangerous, for others, to whom there may be evident no reason for doubting the data; and such work will eventually and inevitably reflect injuriously on its maker.

As regards duplicate analyses, however, it must be remembered that close correspondence in two determinations by the same method is not, in itself, conclusive proof of correctness. It is possible to obtain closely concordant or practically identical results on repetition by poor as well as by good methods; for if the same errors are made, and to about the same amount, in duplicate analyses, the figures in each may agree closely and yet be far from the truth.

At the same time, when poor methods are used or the analyst is incompetent the chances are decidedly against obtaining duplicate results that are so closely concordant as to be satisfactory, particularly if errors in manipulation have been committed; so that, if the methods are good and the analyst is competent, duplicate figures that agree well with each other justify, on the whole, a high degree of confidence in their correctness.

Summation.[1]—In the ideally perfect analysis, of course, the

[1] Various phases of this topic have been discussed by: Fresenius, **2**, p. 168; Hillebrand, p. 27; Mellor, p. 245; M. F. Connor, C. R. **12**, Cong. Geol. Int., p. 889; H. H. Robinson, Am. Jour. Sci., **46**, p. 257, 1916; H. S. Washington, Prof. Paper 99, p. 21.

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summation will be exactly 100 per cent; but in practice, as is well recognized, this result is seldom obtained, and if so it must usually be regarded as due to the compensation of different plus and minus errors.

As Hillebrand has stated, "A complete silicate rock analysis which foots up less than 100 per cent is generally less satisfactory than one which shows a summation somewhat in excess of 100. This is due to several causes. Nearly all reagents, however carefully purified, still contain, or extract from the vessels used, traces of impurities, which are eventually weighed in part with the constituents of the rock. The dust entering an analysis from first to last is very considerable, washings of precipitates may be incomplete, and if large filters are used for small precipitates the former may easily be insufficiently washed."

On the other hand, deficiencies in the summation may be caused by mechanical loss, such as through spilling of drops or blowing away of light powders; or by physico-chemical factors, as the partial solution of slightly soluble precipitates, or the incomplete absorption of carbon dioxide or water. A low summation may also be caused by the non-determination of some constituent.

The correctness of the opinion of Hillebrand and other experienced analysts that the plus errors tend to surpass the minus errors is shown clearly by Robinson's average summation, derived from 3391 analyses. This is 100.13, with a maximum at 100.15–100.19.

The limits of summation below or above 100 per cent which may be considered allowable and consistent with satisfactory work are considered by Hillebrand to be 99.75 and 100.50, and by Mellor, 99.50 and 100.50. For allowable limits appropriate to first-class work by an experienced analyst I am in accord with Hillebrand. But for the usual run of analytical work one may be liberal and fairly extend these limits to 99.50 and 100.75,[1] though the lower limit is, as Hillebrand remarks, rather too low for first-class work, especially in view of the tendency to high summations.

If the analyst obtains a summation between these limits he may consider his results as satisfactory, provided that there is no reason to suspect errors having been made that compensate each other. For the student must realize that a summation of nearly

[1] Cf. Washington, Prof. Paper 99, p. 21.

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or exactly 100 per cent is not conclusive evidence of accurate work, because of this possible balancing of plus and minus errors.

If the analysis foots up under the lower limit, especially in several analyses of a series of similar rocks, there is strong probability that some constituent has been overlooked or some systematic error has been committed. In this case, or if the summation is above 100.75, the analysis should be repeated in whole or in part. As Hillebrand remarks: "It is not proper to assume that the excess (or deficiency) is distributed over all the determined constituents. It is quite as likely, in fact more than likely, to affect a single determination and one which may be of importance in a critical study of the rock from the petrographic side."

There are several special cases of high or low summation that are connected with the determination of various constituents, and which do not, in themselves, indicate inferiority of the analysis as a whole.

If water be determined by loss on ignition the summation will usually be lower than it would be were the water determined directly. This is because of the partial oxidation of the ferrous oxide in the rock, and a consequent gain in weight, the algebraic sum of this and the actual loss of water producing an apparent amount of water less than that which is really present.

If the iron oxides are not separately determined, but are given as ferric oxide, the summation will be too high by one-ninth of the amount of ferrous oxide present; and, conversely, if they are given as ferrous oxide alone, the summation will be too low by one-tenth of the ferric oxide present.[1] This error is, of course, eliminated if both oxides are determined correctly.

If the analysis shows that chlorine, fluorine, or sulphur (as sulphide) are present, an amount of oxygen equivalent to the amounts of these must be deducted, or the summation of the analysis will be too high by that amount. The oxygen equivalent of chlorine is 0.22 of its amount, that of fluorine 0.42, and that of sulphur is 0.43 if this is present only in pyrrhotite. As regards the sulphur of pyrite, the iron with which it is combined will be given as ferric oxide in the statement of the analysis, although

[1] The molecular weight of Fe_2O_3 is 160 and that of $2FeO$ is 144, the difference (the weight of one atom of oxygen) being one-tenth of the former and one-ninth of the latter.

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Hillebrand has shown that the mineral is attacked by sulphuric and hydrofluoric acids to only a scarcely appreciable extent in the determination of ferrous oxide. Consequently the oxygen equivalent of sulphur in pyrite is 0.375, instead of 0.25, as it would be were its iron content determined as ferrous oxide.

To give an example of the application of these corrections: if the sum of an analysis is 100.28 and there is 0.54 Cl present, we must deduct $0.54 \times 0.22 = 0.12$, leaving 100.16 as the correct summation. The corrections for fluorine and sulphur will seldom be called for.

In the earlier days of analysis both chemists and petrographers were content with very poor summations, even with those which fell below 99.00 or above 101.00. It is to be regretted that the same complacency, though less often met with, is not quite extinct at the present time. The intelligent and conscientious analyst or petrographer should look upon such summations with the gravest suspicion, and reject or remake any analysis that thus furnishes evidence of such manifestly erroneous results, either throughout or in part of the analysis.[1]

4. Weighing out the Portions

There are two methods of weighing out portions of rock powder for analysis; these may be called the method by addition and the method by subtraction.

The method by addition is most generally used and serves best for all the rock portions, except that used for the determination of the alkalies. The previously ignited and cooled crucible (covered) is weighed to tenths of a milligram as described previously, and its weight is recorded. A weight equal to that desired, say 1 gram, is added to the right-hand pan. The crucible and its cover are removed from the left-hand pan with the forceps, the crucible (uncovered) being placed on the table in front of the balance case. A little of the rock powder is carefully removed from the specimen tube with the platinum spatula and placed in the crucible, taking care to raise as little dust as possible and that none of the powder adheres to the sides of the crucible. The crucible

[1] This subject is discussed at some length in Washington, Prof. Paper 99, pp. 21, 24, 25.

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is then replaced on the left-hand pan, its cover laid on, and the pans and arms gently released. If there is not enough powder to slightly more than outweigh the added weight, a little more is added, or if there is too great an excess of powder, a little is taken out with the platinum spatula; the crucible being, in either case, removed from the pan and placed on the table, so that none of the powder may fall upon the pan. This is continued until there is in the crucible a weight of powder but slightly (say about 1 centigram) more than the added weight. The correct weight is then taken to one-tenth of a milligram as before. With a little experience one is soon able to judge quite well when there is about the right amount of powder, allowance being made for the different specific gravities of different rocks.[1] Also, one will soon be able to judge from the movements of the pointer whether the difference in weights on either pan is great or not.

The method by subtraction is used for weighing out the portion for the alkali determination, as well as when substances have to be weighed out accurately to make up standard solutions, as with sodium oxalate. The specimen tube containing the powder is wiped perfectly dry and uncorked, and is then placed on the left-hand pan of the balance. It is well to support it in a light metal tube stand, so as to prevent its rolling. In handling the tube during the weighing it is scarcely necessary to use a dry handkerchief or test-tube holder, as little or no appreciable error is introduced if the fingers are perfectly dry.

When it has been weighed, the requisite weight (say one-half a gram) is removed from the right-hand pan, and an amount of powder about equal to this is very carefully poured out into the proper receptacle, which will be the platinum basin with the alkali determination (p. 195). This pouring must be done with the greatest care, and the mouth of the tube is to be held close to the bottom of the basin, so as to prevent loss of powder. During the pouring, also, the breathing should not be directed toward the basin, or some of the powder may be blown out.

When about a sufficient amount has been poured out[2] the

[1] Thus, a one-gram heap of basalt powder is distinctly smaller than one of granite.

[2] The beginner would better proceed cautiously and pour out at first what is evidently too little.

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mouth of the tube is tilted up (still above the basin), and the sloping tube is gently turned around on its axis, and possibly tapped very lightly, so as to bring the remaining powder away from the mouth and toward the bottom of the tube without loss. The basin is covered with a watch-glass, and the tube, still uncorked, is weighed as before. The loss in weight is the weight of powder taken for analysis.

It may be necessary to pour out several additional small portions so as to get the amount that is needed. A small excess, say of a few centigrams, or even a decigram, will be of no consequence in the alkali determination. But if one has poured out too great an excess, this cannot be corrected by replacing some of the powder in the tube, because some of it would inevitably be lost. If this happens all of the powder is to be replaced in the tube, the basin is wiped clean and dry, and the operation is begun over again.

5. Fusion with Sodium Carbonate [1]

For the determination of silica, alumina, total iron oxides, titanium dioxide, lime and magnesia, in what is called the "main portion," decomposition may be effected by several fluxes, as has been mentioned on p. 85. Of these, sodium carbonate is, for general use, by far the best and the one most often used. It is used exclusively, indeed, for this purpose by the chemists of the U. S. Geological Survey and by myself. It will, therefore, be the only one to be considered here.

The Fusion.—The method of fusion with sodium carbonate owes its usefulness to the fact that this reagent at the temperature of fusion decomposes the minerals present, forming silicate, aluminate, titanate, phosphate and zirconate of sodium, and carbonates, silicates, and possibly aluminates, of iron, manganese, magnesium, calcium and barium, all of which are readily soluble in hydrochloric acid.

About 1 gram of rock powder is generally used for this operation. A platinum crucible of 35 or 40 c.c. capacity is selected. A smaller one is not appropriate on account of danger of loss through bubbling of the melted mass, as well as on account of greater dif-

[1] Classen, **2**, p. 608; Hillebrand, pp. 87–90; Mellor, pp. 163–166; Ostwald, p. 218; Treadwell, **2**, pp. 488–489.

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ficulty in loosening the solid cake. For this fusion, the sides of the crucible should have considerable flare, and one with vertical sides is unsuitable. The crucible used for this fusion must be hard and not easily dented or bent. It should, therefore, be of platinum alloyed with iridium or of palau (which I have found to answer very well), but not of pure platinum, which is much too soft. Any loss in weight upon ignition is of no consequence here, as the crucible is not weighed both before and after fusion, and it may be reserved for this purpose.

The crucible is cleaned, ignited to bright redness, placed in the desiccator after it has cooled below a red heat, and allowed to cool. When perfectly cold, it is weighed with the cover on, the weighing being carried to tenths of a milligram by means of the rider, and the weight noted. This weighing is carried out according to the directions given on pp. 129–131, and the weighing out of the powder is carried out in the manner just described.

It is not necessary, indeed it is better not, to weigh out exactly 1 gram, which will take considerable time, but an amount varying from 0.9 to 1.1 gram should be taken, preferably a little more than a little less than a gram. With some practice it will be found simple to estimate with the eye when one has about the right amount.

The crucible (covered) and the weights being removed from the balance, one of a pair of balanced 3-inch watch-glasses is placed on the right-hand pan, and a 5-gram weight placed on it. On the other watch-glass, dry, powdered, anhydrous sodium carbonate is placed by means of a dry horn spoon, which is kept for this purpose in the balance-case drawer, and which must be carefully wiped off at the end of the operation. Enough is added or subtracted to balance the other watch-glass and the 5-gram weight. The addition or subtraction is to be done with the watch-glass on the table, not on the pan, lest some of the carbonate get on the latter. It is not necessary to weigh the carbonate accurately, but the difference should not be more than a few decigrams either way. It is usually stated that the amount of carbonate should be four times that of the substance taken, but it is found that a somewhat larger amount is advisable for proper fusion, and for very basic rocks as much as 6 grams may be taken advantageously, as with these the decomposition is less easy.

The crucible is placed on a clean sheet of paper, the cover

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laid to one side, and the greater part of the sodium carbonate is transferred to the crucible by means of the platinum spatula, care being taken that none of the rock powder is thrown out. About half a gram of carbonate should be left on the watch-glass.

The mixing of the rock powder with the carbonate and the process of fusion have been described on (pp. 86–87). As, however, this fusion is of primary importance, it will be well to repeat here the description of the operation.

The flux and powder in the crucible are thoroughly mixed by stirring them gently with the broad end of the dry platinum spatula, this being done so that there is no loss of powder. They should be so intimately mixed that the mass appears homogeneous to the eye, and particular care should be paid to getting the carbonate well down and around all the corners, so that no patches of unmixed rock powder remain at the bottom, where they would be attacked slowly and with difficulty.

When the powders are intimately mixed and smoothed down, the spatula is cleaned of any adherent mixture by rubbing on the portion of carbonate that remains on the watch-glass. This portion is then added to the mixture in the crucible.

The covered crucible is then placed vertically in a triangle, and is heated at a height of about 10 cm. above a low Bunsen burner flame for five to ten minutes, so that any moisture may be expelled. It is then gently lowered until the bottom is a faint red, and is kept thus for another five minutes or so. The flame is then gradually raised until the mass is in a state of quiet fusion. If the operation is conducted with proper care and slowness, all the carbon dioxide, formed in the reaction between the silicates and carbonate, can be driven off quietly through the half-sintered mass and without any spattering.

When the mass is in fusion the height of the flame and of the crucible above it are so adjusted that the mass is liquid and of a dull red (about 850°), but without any spattering of drops onto the cover. The crucible is to be kept covered during the operation, except for examination of the contents. This will demand some attention the first few times the operation is done, but the right conditions are soon learned with practice and care. The melt is to be kept in this state of quiet fusion for at least fifteen minutes, during which slow currents can be observed to cross it, which

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resemble those in a quiet lava-filled crater, such as that of Kilauea.

The liquid will, with some rocks, not be perfectly clear and transparent, as the carbonates of iron, calcium, and magnesium will form cloudy masses within it; so that any such appearance need not cause concern. Indeed, with rocks that are very high in lime, magnesia, and the iron oxides, the mass may appear to be only half fused, because of the abundance of these substances, although the rock is, in reality, completely decomposed. Some sodium carbonate will usually vaporize and condense on the under side of the cover, but this is of no consequence.

When the whole operation has lasted from the beginning at least one-half to three-quarters of an hour, and it is judged that decomposition is complete, the crucible is taken from the flame and is placed on a clean, cool flat surface of iron or polished stone. Such methods for quick cooling as using a blast of air, or dipping into water, are never to be used, as they injure the crucible and greatly shorten its life. They also make impossible a neat removal of the cake from the crucible. Hillebrand recommends giving the crucible a quick rotary motion before placing on the slab, so as to spread the melt over the sides in a thin sheet. This certainly has the advantage of rendering the subsequent disintegration more rapid, and also to some extent facilitates the separation of the cake from the crucible. It is not, however, necessary, and in general I am content to cool the crucible quickly but quietly on a slab of polished granite.

During the first moments of cooling the melt should be watched, and if it bubbles or forms miniature craters, this may be taken as evidence that the decomposition and the expulsion of CO_2 are not complete. In this case the whole should be remelted and kept at a bright-red heat for another ten minutes.

It is very important that the crucible and its contents be *thoroughly cold* before the removal of the cake is begun. The contents must be so cold that they separate either wholly or partially from the metal walls. If water is poured into the crucible before the cake is thoroughly cold, the removal of the cake will probably be difficult. It is always better to be patient during the cooling process and to allow the crucible to stand more time than

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may be actually needed, than to incur the possible annoyance of a cake that obstinately refuses to be extricated.

When a considerable amount of pyrite is present in the rock, it is necessary to oxidize the sulphur, to avoid attacking the crucible. This may be done by adding a very little potassium nitrate to the carbonates. But even a small quantity of this gives rise to effervescence, through reaction with the carbonates, and hence increases the possibility of loss through spattering. There is also danger of attacking the crucible through the action of the nitrate. It is, therefore, better after weighing the rock powder and before the addition of the alkali carbonate, to roast the rock powder in the open crucible at a low red heat, insufficient to sinter, and far less to fuse, the rock. The mass can then be mixed with the carbonates and the fusion proceeded with, as described above.

As a general rule the cold cake will be of a bluish-green color, due to the formation of sodium manganate. It sometimes happens that rocks high in ferrous oxide, even if containing considerable manganese, show in the cooled melt not a trace of the characteristic green, but only a muddy-brown color, due to disseminated ferric compounds.

Hillebrand attributes certain irregularities in the coloration to the presence of a reducing atmosphere within the crucible, under conditions which are little understood. Thus it may happen that " two fusions made side by side or successively, under apparently similar conditions, may in one case show little or no manganese, in the other considerable." It is probable that all rock analysts have had similar experiences.

Removal of the Cake.—Before describing the removal of the cake from the crucible, one or two points in regard to the crucible itself may be touched on. From a new or little-used platinum crucible, with the ordinary amount of flare, the extraction of the cake usually offers no special difficulties, if attention be paid to the small points mentioned above and given below. But after a platinum crucible has been in use for some time, especially when it is often heated over the blast, the bottom tends to drop, and so alters the shape of the lower part. The smooth, single, interior concave curve becomes a double, ogee-like one, and, being slightly convex inwardly, frequently gives rise to difficulty in removing the cake. When the crucible which is used for the carbonate

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fusion gets into this condition, it is well to return it to the maker and have it re-formed.

As all dents and other irregularities are sure to cause difficulty, the platinum crucible should never be allowed to fall or become dented. Above all, any squeezing or other violent pressure should be avoided in attempting to loosen the melt, as any such deformations will greatly decrease the usefulness and value of the crucible. Caution on these points may seem superfluous, but one so often sees battered crucibles in use in laboratories, especially in the hands of students, that the reference to them may not be amiss.

The thoroughly cold crucible containing the cake is placed in a platinum triangle and nearly half filled with water. After standing for a minute, so as to allow the water to creep below the cake, it is gently heated over a small flame. The flame is cautiously applied, especially around the edges of the cake, boiling being avoided as likely to lead to loss. After the edges are freed, the bottom is gently heated, when, under favorable circumstances, the cake loosens. If this first operation is not successful, the fluid is carefully poured out into the platinum basin, any drops running over the edge being washed into the basin with a little water from the wash-bottle. The crucible is then again half filled with water, and the operation repeated. Two or three repetitions will usually be sufficient to attain the object. An undamaged, smooth crucible, patience, and gentle heating are the prime requisites for success in this operation; the opposites are disastrous.

When the cake is loosened it is transferred to the platinum basin. The crucible is washed slightly, so as to transfer any loose particles to the basin. Small fragments of the melt may still adhere to the sides of the crucible; these will be removed by subsequent treatment. The crucible is therefore covered and set aside. The platinum basin (covered) containing the cake, and not more than one-third filled with water, is heated on the water-bath, or over a low flame, so as to avoid boiling, until the cake is easily broken up with the spatula, and it is finally more or less disintegrated. It is not necessary, nor is it possible, to dissolve the cake entirely in the water, but it is advantageous that it be somewhat disintegrated, as this will facilitate the solution in

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hydrochloric acid.[1] The presence of a few small, black grains (of magnetite or ilmenite) need not cause uneasiness, as they are attacked with difficulty by the carbonate, but will be dissolved by the acid.

If the cake should prove obstinate and refuse to loosen from the crucible, one of two plans may be followed. The one preferred is to dissolve the cake in the crucible itself over a low flame or on the water-bath. The liquid in the platinum basin may be used for this operation, in small portions at a time, the crucible being emptied back each time. The other consists in placing the crucible on its side in the basin, filling this with water about one-third full, and heating gently till the cake is dissolved. The crucible is then lifted out of the basin by means of a stirring-rod, and thoroughly washed, while held on the rod above the basin, inside and out, the washings falling, of course, into the basin.

Solution of the Cake.—If the cake is green, chlorine will be evolved, on the addition of hydrochloric acid, through reaction with the manganate, and will attack the platinum. To avoid this a few cubic centimeters of alcohol are added to reduce the manganate. It is best always to add a little alcohol.

When the cake is disintegrated, the platinum spatula is removed and washed with a little water into the basin, and laid aside in a clean place. The basin is removed from the flame and covered with a watch-glass, which should project about one-half an inch on all sides. This is, of course, placed with the convex side down, as must always be done with covering watch-glasses. Fifteen or 20 c.c. of a concentrated hydrochloric acid are measured off in a 25-c.c. measuring-cylinder with lip, and poured very gradually into the basin through a small funnel, the end of which has been somewhat drawn out and bent at an angle of 45°, so as to project into the basin through the lip-opening. This addition of acid should be very gradual, by a few drops at a time at first, so as to allow the effervescence to be as gentle as possible. It is also well to let the acid flow down the side of the basin below the lip, so that the drops thrown up by the first, somewhat violent, effervescence

[1] While this disintegration in hot water is generally recommended, it is not necessary, and time will usually be saved by decomposing the cake directly with hydrochloric acid. It should then be rubbed occasionally with the platinum spatula so as to facilitate solution.

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may be directed away from the lip-opening. A pink blush, due to $MnCl_2$, indicates the presence of considerable manganese.

When all the acid has been added except 1 or 2 c.c. the tip of the funnel is washed into the crucible with a little water, and the funnel is withdrawn. A few drops of acid are poured on the under side of the crucible cover, to dissolve any drops spattered from the fusion, and washed into the crucible with a very little water. The rest of the acid is then poured into the crucible, to dissolve any adhering portions of the carbonate, and slightly warmed, the crucible being covered.

The basin (covered) is heated for ten minutes or so on the water-bath, to expedite solution in the acid, and to drive off carbon dioxide. When all effervescence has ceased in the basin, this is removed from the water-bath, the drops on the watch-glass cover are rinsed down into it, the glass being held vertically, with the part which has been next the lip downward and near the surface of the liquid in the basin. The rinsing is to be repeated several times, the stream being so directed as to let the water flow over all the wetted surface from top to bottom. The watch-glass is laid aside, and the sides of the basin above the liquid are washed down by a gentle stream from the wash-bottle, the basin being slowly revolved to facilitate the operation. One complete washing down all around will be sufficient. The contents of the crucible are then added, and this and the cover rinsed several times into the basin. When the operation is complete, if care has been used to avoid an inordinate amount of wash-water, the basin should be little more than half full.

As a little silica adheres persistently to the crucible the inside of this is to be rubbed with a small piece of moist filter paper, which is then thrown into the basin. This is disintegrated during the evaporation.

The platinum spatula is then put in the basin, resting in the lip, and this placed uncovered on the water-bath for evaporation. The fluid should be clear, and contain no solid except possibly some light particles of silica. There may be a few small black particles of magnetite or ilmenite present, which will dissolve in the hot acid. But if small, hard, gritty particles are felt, by the spatula, at the bottom, the fusion has not been successfully carried out to complete decomposition of the rock, and the contents

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of the basin should be rejected, another portion of rock powder weighed out, and the whole operation of fusion with sodium carbonate gone through with as before. This should never happen, and is easily avoided by sufficiently long fusion with the sodium carbonate.

6. Silica[1]

The fluid in the basin now contains all the rock constituents in solution as chlorides, except the silica, which is for the most part in solution as a soluble silicic acid, and partly as insoluble particles. Our first object then is to separate the silica from the other constituents, so that it may be weighed. This is effected by evaporation to dryness, whereby the silica is rendered insoluble in water.

Errors.—It has been shown by Hillebrand and others that a single evaporation does not render all the silica insoluble; so that two, or even three, evaporations are necessary for accurate work. Prolonged heating at 110°–130° is apt to allow some of the silica to be dissolved in the hydrochloric acid used, as well as to increase the impurities in the silica. This is due to recombination of the silica with some of the bases, mostly either with magnesia or with soda.

Complete dehydration of the silica is somewhat uncertain and is apt to be incomplete, and unless the silica is ignited at a very high temperature it is apt to be hygroscopic. Blasting for twenty minutes or more is therefore generally recommended. Although this may be advisable, it may cause loss in weight of the crucible, and for general work I find that strong ignition over a good Meker flame for twenty minutes gives satisfactory results. This is probably due to the compensation for the slightly imperfect dehydration by the small amount of silica that goes into solution and that is not recovered with the alumina.

A small amount of silica adheres strongly to the basin and will be lost if it is not rubbed off. It would appear to be almost impossible to remove this silica from porcelain with a " policeman."[2]

[1] Classen, **2**, pp. 605–611; Fresenius, **1**, pp. 509–511; Hillebrand, pp. 91–97; Mellor, pp. 166–167; Treadwell, **2**, pp. 485–488; Lenher and Truog, Jour. Am. Chem. Soc., **38**, p. 1059, 1916.

[2] Cf. Hillebrand, Jour. Am. Chem. Soc., **28**, p. 232, 1906.

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Practically all the silica that is not rendered insoluble in the main evaporations is precipitated with the alumina, and must be recovered from the solution of the fusion of the alumina precipitate in pyrosulphate, though a little of it is lost here, as silica is slightly soluble in this reagent. The amount, however, is always small.

The weight of silica must always be corrected for the impurities that it invariably contains, by evaporation with hydrofluoric acid.

From the possible errors just given it may appear that the correct determination of silica is so fraught with difficulty and uncertainty, as to be probably unsatisfactory. This conclusion, however, is not borne out by the facts. In the first place, the actual error caused by each of these possible sources of error is generally very small, with the exception of that due to impurity in the silica which can be eliminated, however, by evaporation with hydrofluoric acid. Secondly, the errors apply to that constituent which is present in by far the largest percentage in the great majority of rocks, and so they are of comparatively insignificant influence. Indeed, much crictical study of the character and value of rock analyses has led to the conclusion that, in analyses not of the best quality, the figures for silica (and lime) are more likely to be nearly correct than those of the other constituents.

Separation of Silica.—To render the silica insoluble, the solution in hydrochloric acid of the cake from the sodium carbonate fusion is evaporated to dryness in the platinum basin.[1] This is carried out on the water- or steam-bath until no more fumes of hydrochloric acid are given off and the mass appears to be quite dry, the dark-yellow color of the moist salts changing to a pale-brown shade. During the last stages it is well every now and then to break up the gelatinous mass with the platinum spatula, which is kept in the basin, so that the water and hydrochloric acid may pass off more readily. When the mass becomes crystalline, the lumps may likewise be broken up, but this should be done with caution to avoid loss by flying off of particles of the salts.

It is recommended by some that the dry salts be heated for some time at a temperature of 110° or 120°. This, however, is highly disadvantageous and should not be done, as apparently sili-

[1] A porcelain basin may be used, but it is less satisfactory, as it is liable to contaminate the liquid, and because it is difficult to remove the silica completely from the porcelain surface. A glass basin must not be used.

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cates are apt to be formed that are soluble in hydrochloric acid and so lead to loss of silica. At the same time the prolonged heating will probably add considerably to the impurities in the silica.

After half an hour's further heating on the water-bath, when the mass is dry,[1] the basin is removed from the water-bath and the contents are moistened with 5–10 c.c. of concentrated hydrochloric acid, to dissolve the basic salts of alumina, iron, and magnesia that are formed during the evaporation. The small amount of salts on the spatula are also moistened with the acid. The mass of salts should be made only pasty with the acid, as too much will tend to prolong the filtration, and silica is appreciably soluble in strong hydrochloric acid. The pasty mass is mixed thoroughly with the spatula, some of it being rubbed around the line that marks the original border of the liquid, where a zone of strongly adherent silica is apt to be formed.

Water is now added from the wash-bottle, the stream washing down the sides of the basin. About 15–20 c.c. of water in all should be added. The spatula is rinsed off into the basin, and is cleaned with a bit of filter paper which is dropped into the basin, because a little silica (only visible when the spatula is dry), adheres to it persistently. The basin should not be more than one-third, at the most, full of liquid.

A glass stirring-rod, about 1 inch longer than the diameter of the basin, is placed in this, and the contents are heated on the water-bath or over a low flame, with constant stirring, until the chlorides are entirely dissolved and only insoluble silica remains. This is indicated by the absence of gritty particles of salt on "feeling" with the rod.

While the solution of the chlorides is being effected at a gentle heat the filter may be made ready. A 9-cm. filter and a 6½-cm. funnel are used. The filtration is carried out as described on p. 118, a 400-c.c. beaker being used to catch the filtrate.

When all the liquid and silica that will pass readily with it

[1] Mellor (p. 175, note 3) suggests the addition of alcohol before drying, so as to hasten the process. I have used this for some years in the drying of the chlorides in the alkali determination (p. 199) with good results, and I think that it would aid in the dehydration of the silica also. A few cubic centimeters may be added when the crystalline mass is almost dry and the drying is then continued to completion.

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have been brought on the filter, the basin is gently rinsed with a little cold water from the wash-bottle, the silica adhering to the sides being washed down to the bottom, and the liquid and as much of the silica as possible are poured into the filter as before. When the filter is empty, the basin is held in the left hand, above the filter, with the stirring-rod across it and resting on the lip, the end of the rod an inch or so beyond, and the rod kept in place by the tip of the left forefinger. A gentle stream of water is then directed against the now upper side of the basin, so as to wash the silica into the filter, and at the same time rinse the basin. When the filter is nearly full the liquid is allowed to empty and the operation repeated until the silica is washed thoroughly, and all the silica brought into the filter as far as possible without too many rinsings. The stirring-rod is washed off into the beaker.

The water used in washing the silica should be cold, that is at room temperature, or better containing a little hydrochloric acid. This is because hot solutions of alumina and iron, unless decidedly acid, hydrolyze readily and throw down basic salts that contaminate the silica. It may happen that the silica becomes brick-red from the iron present if it is washed with hot water that contains no acid

Lenher and Truog[1] recommend using hot water containing 5 per cent (by volume) of hydrochloric acid. This has the advantages of diminishing the time and volume of liquid needed for washing, helping to remove the bases and basic salts present in the silica, and also preventing the silica from going into a colloidal condition and so passing through the filter. Their suggestion may well be adopted. In this case, pure hot water from the wash-bottle may be used, and a little hydrochloric acid added to the contents of the filter with each addition of the wash water.

When the liquid has ceased dropping from the last rinsing, the platinum basin is substituted for the beaker beneath the suction-tube, taking care to lose no drops from the latter during the change. The contents of the beaker are poured into the basin, and the beaker itself is rinsed once or twice, not more, the rinsings going also into the basin. The beaker and basin are then interchanged once more, and the stirring-rod is placed in the beaker

[1] Lenher and Truog, Jour. Am. Chem. Soc., **38**, p. 1058, 1916. Hillebrand, (p. 92) does not recommend this.

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set beneath the funnel. The basin with the platinum spatula in it, is once more placed on the water-bath for the second evaporation.

While the second evaporation is going on the washing of the main portion of silica with hot, slightly acid water is completed. The filtrate is received in the 400-c.c. beaker previously used. The portions of wash water added each time should be small, so as to keep the volume of filtrate down.

When the second evaporation is complete and the salts are reduced to dryness and free from HCl, occasional stirring with the spatula hastening the process, the mass is again moistened with a little (3–5 c.c.) hydrochloric acid, and, after standing (warm) five minutes, about 50 c.c. of water are added, and the whole gently heated to complete solution (except for particles of silica).

The liquid is then filtered through a separate 7-cm. filter, the basin is well rinsed, and the filtrate and washings caught in the 400-c.c. beaker containing the previous filtrate. The small amount of silica is to be brought into the filter, and the basin rubbed with a small piece of moist filter paper to remove adherent silica. There will be need of but little washing for this portion. Hot water containing about 5 per cent of hydrochloric acid may be used.

When washing is complete the bulk of liquid, including all the washings, in the 400-c.c. beaker should not be more than 200 c.c., if the operation has been conducted with care and due avoidance of excessive use of liquid.

Ignition of Silica.—A platinum crucible of 25 or 35 c.c. capacity is selected, preferably the latter if the rock contains much alumina or iron, ignited, cooled in the desiccator and weighed. The second filter, that contains the extra silica from the second evaporation, is removed from the funnel with the platinum spatula, placed in the crucible, heated until the paper is carbonized, and then reduced to ash. This will take but ten minutes or so.

When the crucible is cold, the free edges of the first filter, that contains the main portion of silica, are folded down on the silica so as to enclose this completely, the platinum spatula being used for this. The little package is then transferred with the spatula to the crucible, placed above the ashes in it, and preferably with

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the side uppermost that has three thicknesses of paper. The package is very gently worked and pressed down toward the bottom of the crucible, but the paper should not be torn, nor should all egress for steam from below be shut off. With a small piece of filter paper any particles of silica adhering to the spatula are rubbed off, and also any which may be on the funnel above the edge of the filter, and the piece of paper is also placed in the crucible. In this way the silica can be dried in the crucible and ignited, with no danger of loss from whirling up of the light powder.

The covered crucible (vertical) is first heated at about 15 cm. above a low flame, the heating being cautious so as to avoid boiling of the pasty mass, and probable loss of substance or spattering of it on the sides of the crucible. This is continued till the contents are dry and the filter begins to char. As the water is driven off the crucible is gradually lowered, but this must be done with great caution, and the flame kept small. A filter which is carbonized at a low temperature is more easily incinerated than one which is carbonized rapidly and at a high temperature. The crucible is finally brought close to the flame and heated till no more smoke is given off. The escaping vapors should never be allowed to ignite, and consequently the flame should be kept low and the bottom of the crucible should not be brought to a red heat till carbonization is complete.

The almost full flame is then turned on and the crucible heated to a bright-red heat, being kept vertical and with the cover very slightly moved to one side, so as to allow the entrance of some air, but not enough to give rise to dangerous draughts. The flame, of course, should not be allowed to envelop the crucible, as an oxidizing atmosphere within it is essential. When the carbon is entirely consumed, or almost so, the cover is put in place, a Meker substituted for the Bunsen burner, and the crucible is heated to a bright red for at least thirty minutes. This is necessary in order to effect complete dehydration of the silica, the last portions of water being retained with great tenacity. It also has the advantage of rendering the silica non-hygroscopic. It is well to reheat the crucible once or twice to constant weight. The cover should be examined to see if it carries any adhering carbon, and if so this is to be burnt off by heating in the flame.

The crucible and its contents are then cooled in the desiccator

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and weighed. The result is to be recorded as Cruc.+SiO_2+x, above the weight of the empty crucible, and also on the same line to the right of it.

The silica as thus obtained is never pure, but contains small amounts of Al_2O_3, Fe_2O_3, TiO_2, P_2O_5, and possibly other impurities. In " basic " rocks these may amount to one-half of one per cent or more. The correction of silica for these must not be omitted on any account, no matter what may be the kind of rock or silicate.

After weighing, therefore, the silica is moistened with 1 or 2 c.c. of water. In doing this the tip of the wash-bottle should be filled with water by blowing before inserting in the crucible, to avoid blowing out any of the light silica by the first puff of air from the empty tip. The stream is directed against the side of the crucible, the tip being inserted below the slightly raised cover.

Three or four drops of dilute sulphuric acid are then added, this being necessary to retain the TiO_2, some of which would be vaporized as titanium fluoride in the absence of sulphuric acid. Hydrofluoric acid is then poured in, a few drops at a time. The action is apt to be violent, but with care and sufficient moistening of the silica no loss need be incurred. The hydrofluoric acid should be added in quantity sufficient to dissolve all the silica on warming. Five, or at most 10 c.c. should be ample for this purpose.

The crucible is then placed in the triangle of a radiator, such as is described and figured by Hillebrand.[1] If this is not available, a capacious (50- or 60-c.c.) nickel[2] crucible, with an appropriate triangle made of nickel or platinum wire, serves admirably. The triangle is bent or spread out, so that the platinum crucible is well down in the radiator, but with the sides not touching. This arrangement assures uniform heating of the liquid and, with care, prevents " creeping " or loss by spattering. The radiator and crucible within it are heated over a moderately low flame, so that the liquid never boils, until the contents are nearly dry. Toward the end, when only a few drops of sulphuric acid are left, the operation can be hastened by cautiously heating the bottom of the

[1] Hillebrand, p. 31.

[2] A porcelain crucible may be used if one of nickel is not at hand, but the evaporation is not so rapid.

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naked platinum crucible with a small flame waved beneath it until all the acid is driven off. The whole of this operation must be conducted under a hood that is provided with a good draught.

The crucible is then ignited at a bright-red heat, blasting for a few minutes being advisable to ensure the decomposition of the sulphates of iron and titanium, and the complete expulsion of all traces of sulphuric acid. After cooling in the desiccator the crucible is weighed, and its weight noted as Cruc.$+x$ below that of Cruc.$+SiO_2+x$. To this weight of silica is to be added later that of the small portion that is recovered from the pyrosulphate fusion (p. 162), before the percentage of silica can be correctly calculated.

As pointed out by Hillebrand, the composition of this residue is variable. It always contains alumina, and ferric, titanic and phosphoric oxides, very exceptionally baryta, but no lime or magnesia if the rock has been properly decomposed. The assumption that all the titanium is present in this, or that the residue consists almost only of TiO_2, is quite unwarranted.

The crucible containing the impurities in the silica may be laid aside in a desiccator or other safe place, *uncleaned*, for use in the subsequent ignition of the precipitate of alumina, etc. (p. 157).

7. Alumina Precipitate

The filtrate from the silica contains, of the main constituents, the aluminum, iron, titanium, manganese, zirconium, and phosphorus oxides, which are conjointly separated from the lime, magnesia, and alkalies also present, by precipitation with ammonia water. An alternate method is precipitation with sodium acetate, but, for general purposes, this is much inferior to the other. The ammonia precipitation will, therefore, be described first, and a brief description of the " basic acetate " method will follow.

It should also be noted that this filtrate contains some platinum.[1] Some of this comes from the crucible in which the sodium carbonate fusion has been made. Sodium carbonate loses a little carbon dioxide on heating, even at 800°, and experiments by E. G. Zies in the Geophysical Laboratory indicate that it is the sodium oxide so formed that attacks the platinum. The greater

[1] Cf. Hillebrand, p. 97; Treadwell, pp. 110, 493.

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part comes from the platinum basin in which the evaporation to dryness has been carried out. Ferric chloride is reduced to ferrous by digestion with platinum, which forms chloroplatinic acid. This action will be the greater the more iron the rock contains. It is not necessary to remove this platinum before precipitation with either ammonia or sodium acetate.

Errors in Alumina.—Of all the determinations of chemical constituents of rocks, that of alumina is the most liable to error, not only in magnitude but in variety. This is due in part to its amphoteric character;[1] in part to the gel-like consistence of its hydroxide, and consequent tendency to adsorption of salts and difficulty in washing, as well as its liability to pass through the filter; in part to the tendency of magnesia to be precipitated with it; in large part to the present necessity of determining alumina by difference (as no method is yet known for the satisfactory complete separation of alumina from all other constituents or for its direct determination), so that errors committed elsewhere fall on it; and in part to other causes.

The correct determination of alumina is, undoubtedly more troublesome and difficult than that of any of the other constituents, and errors incidental to it have caused the rejection of many otherwise fairly good analyses.[2]

Especial care must, therefore, be taken in all the manipulations and precautions that are involved in the determination of the various other constituents that are weighed with it. On the whole, the tendency is toward a plus error in its determination.

Although the remarks above and the following list of errors may appear formidable and tend to discouragement, yet, as a matter of fact, they should not be so regarded. To the careless or slovenly analyst the determination of alumina is indeed beset with pitfalls; but if the proper precautions are observed the determination of alumina may be carried out with almost as much accuracy as that of the other constituents, in spite of its inevitable tediousness.

If ammonium salts are not present in sufficient amount some magnesia is precipitated with the alumina,[3] thus increasing the

[1] Cf. Stieglitz, 1, pp. 171 ff.

[2] Cf. H. S. Washington, Prof. Paper 99, pp. 14, 17; also Hillebrand, p. 98.

[3] Cf. Ostwald, p. 150; Stieglitz, 1, pp. 168, 170, 191.

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apparent amount of the alumina and diminishing by just as much that of the magnesia. This is a very frequent error especially among the earlier analyses, and is but too often committed at the present day. It is especially liable to occur in rocks that are high in magnesia, and should be carefully guarded against by the analyst; the more so, as this error is very easy to prevent. The analyst must, therefore, be sure that there is an abundance, (even a superabundance), of ammonium salts, either the chloride or the nitrate, in the liquid. The presence of such salts prevents the formation of colloidal solutions and the consequent "running through" the filter of the aluminum and iron hydroxides.

The first precipitate, whether by ammonia or sodium acetate, should always be dissolved and reprecipitated, even if the rock contains but little magnesia. This double precipitation is necessary because of the tendency shown by the gelatinous precipitate to adsorb dissolved salts, so that the first precipitate is invariably contaminated with salts of lime, magnesia, and the alkalies. If the rock is high in magnesia, a second, or even a third, reprecipitation may be necessary to remove these.

If the ammonia water used is not fresh and contains ammonium carbonate, some calcium carbonate will be thrown down with the alumina, and will, of course, increase the apparent amount of alumina and diminish that of the lime to the same extent. The ammonia water should, therefore, before using, be tested with calcium or barium chloride, and if a precipitate forms the ammonia water should be rejected or redistilled from slaked lime.[1]

If ammonia water is kept in a glass bottle, this is sure to be acted on by the alkaline liquid, rendering the ammonia water impure, sometimes even to the extent of showing flakes of silica or partially decomposed glass. Such ammonia water is not uncommon in many laboratories, but should be unhesitatingly rejected as totally unfit for use, even after filtration. For use in good work ammonia water should never be kept in glass, unless this is coated with ceresine. Even here the ammonia is apt to work its way beneath the wax and become impure.

It is best made by passing the gas into ice-cold water contained in a ceresine bottle (p. 48), in which it should be kept. If bought in glass it should be transferred to ceresine as soon as possible.

[1] Cf. Treadwell, **2**, p. 149.

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In very accurate work the ammonia precipitation should be carried out in vessels of platinum or gold.

If crystalline salts are not present the hydroxides of aluminum and iron tend to form colloidal solutions and pass through the filter. This tendency is less noticeable during the transfer of the precipitate to the filter than during the washing later. It can be prevented by adding ammonium chloride or nitrate to the wash water, and having this hot.

Prolonged boiling or standing after the addition of ammonia is to be avoided, as it tends to make the precipitate slimy and hard to filter, and gives more opportunity for precipitation of lime by the atmospheric carbon dioxide. On prolonged boiling, furthermore, the ammonium chloride present may dissociate, leading to re-solution of some alumina by the hydrochloric acid set free, unless the liquid is sufficiently ammoniacal. On the other hand, ammonia in large excess may, and probably will, dissolve some aluminum hydroxide, which will come down with the lime.[1]

It was formerly [2] recommended that the precipitate be washed entirely free from chlorides, because of the possibility of loss of aluminum and ferric chlorides by volatilization. As regards aluminum, however, it has been shown [3] that there is no such loss, nor, according to Daudt,[4] is there such loss of iron if the amount of ammonium chloride in the precipitate does not exceed about 1 per cent, which, in analytical practice it never should.

If the basic acetate method is used for the first precipitation there is a strong probability that some of the alumina and ferric oxide will not be precipitated, and will pass through the filter. This can be avoided if the conditions as to the amount of free acetic acid are very accurately adjusted, so that care and strict attention should be paid to the suggestions made in the description of the method.

But even under favorable circumstances, and in the hands of experienced analysts, a little alumina is liable to be found in the filtrate, particularly with rocks high in alumina and low in iron.

[1] Cf. Stieglitz, **1**, p. 196.

[2] Second edition, p. 101.

[3] Hillebrand, Bull. 422, p. 99, note *c*; W. Blum, Jour. Am. Chem. Soc., **38**, p. 1294, 1916.

[4] H. W. Daudt, Jour. Ind. Eng. Chem., **7**, p. 847, 1915.

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This should always be recovered before precipitation of the manganous oxide, though this precaution is frequently neglected, apparently through ignorance of the necessity for it. The magnitude of error is usually not very great, but may reach as much as 2 per cent of the rock, judging from some analysis with such abnormally, and otherwise inexplicably, high percentages of manganous oxide.[1]

The basic acetate method should, for these reasons, not be used by the inexperienced analyst, and, unless the use of it is made necessary by the presence of much manganous oxide, it is best avoided altogether in rock analysis, and in any case it should be carried out with the greatest care. It may be noted that nearly all the authorities[2] emphasize the difficulties of the method and even advise against its use.

A further source of error affecting the alumina determination is incomplete reduction of ferric to ferrous iron for the determination of the total iron oxides (p. 162). The unreduced ferric oxide will not affect the permanganate and hence will appear as alumina. The method of separation of alumina from iron, by fusion of the ignited precipitate with sodium hydroxide in a silver crucible, which is sometimes recommended, should never be used. It is open to grave objections and offers no sufficiently compensating advantages.

Precipitation by Ammonium.[3]—To the filtrate from the silica in the 400-c.c. beaker, which should amount to from 150 to 200 c.c. in bulk, 10 c.c. of concentrated hydrochloric acid are added.[4] The object of this is to form ammonium chloride on the addition of ammonia, in sufficient quantity to prevent the precipitation of magnesia along with the alumina and iron. One should also avoid

[1] Cf. H. S. Washington, Prof. Paper 99, pp. 17, 20, 21; 1917.

[2] Fresenius, **1**, p. 647; Classen, **1**, p. 465; Hillebrand, Bull. 422, pp. 100, 113, 116; Jannasch, p. 319; Mellor, pp. 177, 362; Treadwell, **2**, p. 153.

[3] Classen, **1**, p. 562; Fresenius, **1**, pp. 623–625; Hillebrand, pp. 98–103; Mellor, pp. 177–183; Treadwell, **2**, pp. 493–494; H. W. Daudt, Jour. Ind. Eng. Chem., **7**, p. 848; W. Blum, Jour. Am. Chem. Soc., **38**, pp. 1282–1297.

[4] Addition of nitric acid is not necessary, as the ferrous oxide will have been changed to ferric in the fusion and the evaporation. It will be safer, however, to add a few drops. Nor is separation of platinum necessary, as recommended by Treadwell; on the contrary its separation at this stage would be very disadvantageous.

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too large an excess of ammonium chloride, so that for rocks like granites and trachytes, which contain but little magnesia, the addition of 5 c.c. of hydrochloric acid will be sufficient. If the rock is very rich in magnesia 15 c.c. will not be too much.

At this point the analyst has to decide whether or not to precipitate the manganese with the alumina. For accurate work my preference is for the coprecipitation, especially if the rock is rather low in silica and the color of the carbonate melt shows that much manganese is present, because it thus affects the alumina alone and can be corrected for by a separate determination. In this case about one-half gram of solid ammonium persulphate, which has been specially purified, is added to the liquid in the beaker. The manganese will be thrown down as peroxide, but nickel and chromium will remain in solution, the former as an ammonium double salt, and the latter as chromate. Cobalt will be precipitated, but as no more than traces of this are ever present, this is of no moment. Hillebrand [1] points out that if the rock carries appreciable quantities of barium or strontium, or is very rich in lime, the use of the persulphate is not advisable. But two, and certainly three, precipitations will surely get all the lime into the filtrate in any igneous rocks, any barium which may come down can be collected and allowed for later, and it is only in very exceptional cases that the amount of strontium is appreciable here. If the rock is high in silica or is low in manganese (less than 0.20 per cent), as is true of nearly all rocks, the analyst may advantageously dispense with the addition of the persulphate, and disregard the slight error involved in the distribution of the manganese among the alumina, lime and magnesia.

After the addition of the hydrochloric acid (and possibly persulphate), a few drops of methyl orange are added,[2] so as to be able to control the amount of ammonia water added. The liquid is then heated nearly to boiling, when about 50 c.c. of ammonia water are poured into a 100-c.c. beaker [3] and diluted with half as

[1] Hillebrand, p. 102.

[2] Blum (op. cit., p. 1288) recommends either methyl red or rosolic acid. His experiments show that these are better, but for the usual practice the commonly obtainable methyl orange will serve. If nitric acid is used, it must be remembered that this decolorizes methyl orange or methyl red.

[3] This is done to guard against any particles of ceresine finding their way into the liquid. Any present are to be removed.

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much water. This is then poured very slowly and cautiously, and with constant stirring, into the hot liquid. The beaker containing this may be left on the wire gauze, but with the flame removed. Enough ammonia is added to give a slight odor and the liquid allowed to settle a bit. If the clear liquid is still red (acid) a little more ammonia is added until it just turns yellow. If it is yellow, it is best to add hydrochloric acid, drop by drop, to acidity, and then very slightly (2–3 c.c.) more than neutralize with ammonia water. This careful procedure, the principle of which was suggested by Blum, insures the complete precipitation of the alumina and the other constituents with it, and at the same time it prevents the solution of alumina by excess ammonia.

The liquid is then boiled for not more, and better less, than one minute [1] and allowed to cool until the beaker can be handled. It is then filtered, still hot, through an 11-cm. filter placed in a 7.5-cm. funnel, the filtrate being received in an 800-c.c. beaker. This size of filter is appropriate for most rocks, but if the amount of $Al_2O_3+Fe_2O_3$ is much more than 30 per cent it is well to filter through two 9-cm. filters simultaneously, with a 600-c.c. beaker beneath each. The former procedure will be assumed in what follows. It is not necessary to take special precautions against the precipitate passing into the filter, though the greater bulk of the liquid can be generally transferred with but little of the precipitate. Several washings by decantation, as are recommended by some, are not only unnecessary but disadvantageous, as they will add much to the volume of the filtrate.

The beaker is rinsed out only two or three times with hot water, which also serves to wash the precipitate in the filter. This is not to be washed clean at this stage. To prevent the formation of a colloidal solution, a cubic centimeter or so of dilute solution of ammonium chloride should be added to the filter with each addition of wash water. The beaker is not to be cleaned.

After rinsing the beaker, the precipitate in the filter is washed several times with hot water, the stream from the wash-bottle breaking it up more or less. In this operation great care should be taken not to throw too hard or sudden a jet onto the precipitate,

[1] Boiling for longer than this is apt to give rise to the troubles mentioned on p. 149, and, besides, is quite unnecessary. The liquid is apt to bump badly.

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which might easily throw some of it out of the funnel. Complete washing is not necessary at this stage, but the precipitate should be collected in the bottom of the filter, and the upper edges washed clean.

In filtering and washing the ammonia precipitate it is of the highest importance that the mass be not allowed to become dry. Not only will cracks form that permit the wash water to run through without removing soluble salts, but the mass will become hard and difficult or impossible to break up without danger of loss. The transference of the liquid and precipitate to the filter and the washing should, on this account, not be interrupted. This is the filtration, above all the others, to which attention must be paid throughout, and the analyst will soon realize the gain in time and satisfaction in results that come from observance of this precaution. As this first precipitate invariably contains magnesia, as well as some lime and alkalies, its solution and reprecipitation, at least once, are necessary in all cases.

With the platinum spatula a side of the filter is loosened and a channel made between the filter and funnel, so that all the liquid in the suction-tube and tubular part of the funnel may run out into the beaker below. The uncleaned stirring-rod remains in the 400-c.c. beaker and this is placed conveniently near the edge of the table. The funnel is removed from the stand, and with the platinum spatula the filter is gently loosened all around, the edge being turned down as little as possible, and the paper not being torn. The funnel is then held with its side horizontal and the folded part of the filter underneath, the spatula slipped beneath this, and the filter with its contents is carefully removed from the funnel, and placed on the rear inside wall of the 400-c.c. beaker, held sloping in the left hand. The upper edge of the filter should be near the rim of the beaker. The filter is now unfolded, opened out and gently spread and pressed against the glass, which should be accomplished without tearing the paper.

The main mass of the precipitate is pushed down to the bottom of the beaker with the spatula, and this washed off with a few jets of water. About 50 c.c. of water is added, and the filter, that is now adhering to the rear of the beaker, is washed with some warm dilute (1 : 1) nitric acid, poured in several small portions so as to dissolve completely the adherent precipitate, but not disturb the

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filter. More of the acid is added to that in the bottom of beaker, about 25 c.c. in all being ample.

At this point, if but one reprecipitation is to be made, two or three cubic centimeters of a suspension of macerated filter paper (p. 51) is to be added. If another precipitation is to follow, this addition is made before the final one. The addition of macerated paper was first suggested by Dittrich,[1] and is to be recommended. Some experiments by Dr. H. S. Roberts and myself indicate the efficiency of its action. The object of this addition is to distribute fibers of cellulose through the mass of precipitate, so that on ignition the oxides will be left, not as a very hard and tough lump, but in a fine and porous state of division, thus permitting the ready reoxidation of any reduced ferric oxide, and also greatly facilitating the subsequent solution in pyrosulphate.

The liquid is now heated until all the precipitate is dissolved, and, when it is almost boiling, slightly diluted ammonia water is added in very small excess, methyl orange or methyl red being used as an indicator as before. The filter is to be washed down with the ammonia. The ammonia should be added cautiously as the reaction with the heated and rather strong acid is apt to be so violent as to cause loss by spattering.

The contents of the beaker, kept well stirred (the filter still adhering to the back wall), are now filtered through a fresh 11-cm. filter, placed in the funnel previously used, into the original 800-c.c. beaker.

If the rock contains much magnesia or lime, as with the diorites, gabbros, basalts, tephrites, and peridotites, a second solution in nitric acid and reprecipitation is to be made, this being carried out exactly as before, the macerated paper being now added. In this case the washing of the second precipitate need not be thorough. It may occasionally happen that a third reprecipitation is called for, if the rock is exceptionally high in magnesia, or in lime if the persulphate has been used, but this will seldom be necessary.

After the final precipitation, whether it be the second or third, as much of the precipitate as is easily possible is to be got directly on the filter. The sides of the beaker are washed down with strong jets of hot water, so as to loosen the adhering precipitate, but without disturbing the filter or filters spread out

[1] Dittrich, pp. 10, 11, 14.

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over the rear wall of the beaker. The washings, with the precipitate that they carry, are transferred to the filter.

In order to remove the last portions of precipitate, which cling tenaciously to the walls of the beaker, the filter paper hitherto spread on the rear wall is used as a cleaner or "policeman." The lower third of this paper, which is most covered with precipitate, is torn off with the end of the stirring-rod, and is rubbed over that side of the beaker. It is then, along with the loosened precipitate, washed into the filter. Another piece is then torn off and used in the same way, the lower part of the stirring-rod being cleaned by rubbing it against the mass of moist paper in the lip of the beaker. Three or four such rubbings will serve to use up all the previous filters, all portions of which must be got with all the precipitate into the filter in the funnel, and render the interior of the beaker perfectly clean.

The contents of the filter are then washed with many (10 or 12 will usually suffice) portions of hot water, during which the mass is gradually brought down and collected in the lower part of the filter and the upper zone of this cleaned of precipitate. This collection of the precipitate in the bottom of the filter and the cleaning of one-quarter or one-half of a centimeter around the edge is of practical importance, as it greatly facilitates the subsequent transfer to a crucible.

For ordinary work, in a third precipitation only the rinsings and first washings need be caught in the beaker, as the amount of magnesia or lime in the final washings would be inappreciable, and as these washings would add considerably to the bulk of liquid. The contents of the beaker are to be kept (covered) for the determination of lime and magnesia (p. 177).

"Basic Acetate" Precipitation.[1]—The difficulties, uncertainties, and dangers of this method have already been pointed out,[2] and once more is it strongly urged that it be not used, except in some unusual cases, where the ordinary method of precipitation by ammonia will not serve. It is described here, somewhat reluctantly, partly because it may rarely happen to be the best method available, as when there is much manganese present, and

[1] Classen, **1**, p. 465; Fresenius, **1**, p. 647; Hillebrand, p. 100; Mellor, p. 362; Treadwell, **2**, p. 152.

[2] Cf. pp. 149–150.

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because, being a method so often recommended, the description may aid the student in avoiding some of its pitfalls.

To the cold filtrate from the silica, which contains a little free acid, and whose volume is about 200 c.c., a concentrated solution of sodium carbonate is added cautiously till the fluid turns a dark red and a slight turbidity is observed, which does not disappear on stirring. This addition may be made in the beaker covered with a watch-glass, and the solution of carbonate is introduced through the small funnel with bent tip, so as to avoid loss by effervescence. The watch-glass, tip of the funnel, and the sides of the beaker are rinsed down, and if these rinsings are sufficiently acid to redissolve the slight precipitate, as may sometimes happen, a few more drops of carbonate solution are added till a slight permanent precipitate is formed again.

Dilute hydrochloric acid is then added, drop by drop and very cautiously, with constant stirring, till the slight precipitate and turbidity *just* disappear, but the fluid still retains its deep-red color. Especial caution is needed here, as any decided excess will set free enough extra acetic acid from the sodium acetate added subsequently to render the precipitation of alumina and iron incomplete. If too much has been added, therefore, the solution is once more to be slightly more than neutralized with sodium carbonate and again treated with dilute hydrochloric acid more cautiously.

Enough acetic acid of specific gravity 1.044 (33 per cent) is poured in to form about 3 per cent by volume of the total liquid, preferably rather less than more. As the final volume will be about 300 c.c., 8 or at most 10 c.c. of acetic acid are sufficient. If too little is present a slight precipitation of manganese is to be feared, while if too much free acid is present alumina and iron will not be completely thrown down, but will pass in small amount into the filtrate.

About 2 grams of sodium acetate dissolved in a little water are then added. This is the amount for most rocks, but it may be varied somewhat with advantage. Thus for rocks low in the sesquioxides, as granites and rhyolites, $1\frac{1}{2}$ grams may serve, though 2 will not be amiss. But in such rocks as foyaites, phonolites, gabbros, basalts, or tephrites, which contain large amounts of these oxides, the quantity would best be increased to 3 grams, which may be considered the limit.

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If the liquid has not a volume of 300 c.c., it is diluted to this bulk, or to 350 c.c. if the larger amount of sodium acetate has been used. It is heated to boiling and allowed to boil for not more than a minute or two, as prolonged boiling renders the precipitate slimy and difficult to filter. After settling for a few minutes, the liquid is filtered through an 11-cm. filter, and washed only two or three times with hot water. This precipitate, which consists of basic acetates of aluminum and iron, with the titanium, zirconium, chromium and phosphorus of the rock, is rather more apt to run through the filter than the precipitate of hydroxides produced by ammonia. The washing, therefore, should not be thorough, and it is as well to add a little sodium acetate to the hot washing-water, so as to have a crystalline salt present.

After this slight washing the precipitate is dissolved in hydrochloric acid by the method just described, reprecipitated with ammonia water, and this solution and reprecipitation repeated if the rock demands it, exactly as was done in the method by ammonia alone. The final precipitate is to be ignited as described below. It must be remembered, however, that there will probably be another filter containing the alumina and iron which have passed through with the filtrate, so that the ignition of the main portion must wait till this has been incinerated with the extra filters, to avoid reduction of the ferric oxide. Otherwise ignition in a separate crucible and consequently two fusions with potassium pyrosulphate are involved. The filtrate is reserved for the determination of lime and magnesia (p. 177).

Ignition of the Precipitate.—The moist final precipitate in the filter is allowed to drain well and, if time permits, is advantageously kept for half an hour or so, the funnel covered with a filter paper, so as to dry out somewhat. It is then placed moist in the crucible which has been used for the determination of silica, and in which there still remain the impurities left on evaporation with hydrofluoric acid. This is done with the aid of the platinum spatula, the free edges of the filter being folded over inwards, the filter very gently freed from the funnel without tearing the paper, and the whole carefully placed in the crucible with the three-fold portion uppermost. Care should be taken not to soil the sides of the crucible, and to leave abundant free passage for the exit of steam from beneath the mass. The spatula and the interior of

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the funnel are to be cleaned with a small piece of filter paper, which is laid on top of the package in the crucible.

The drying of the moist mass must be done very cautiously, at a considerable height (8 inches or so) above a small flame, the crucible being vertical and covered. Constant watching is necessary at first to prevent any bubbling of the pasty mass, which would soil the upper portion of the crucible with precipitate and render difficult its complete solution in fused pyrosulphate. The crucible is very gently and cautiously lowered as the mass dries off, until the filter is carbonized, when it is heated vertically for a short time at a bright-red heat until the cover is free from adhering carbon.

The crucible is then laid on its side on the platinum triangle, the mouth at the twisted end, and the cover is leant against it, almost vertical, with its upper edge a little below the top of the crucible, leaving a narrow opening above and below.

The flame is directed against the bottom and lower third of the crucible, the flame not being violent enough to cause dangerous draughts, and the incineration of the paper is quickly accomplished. It is then heated at a bright-red heat for at least twenty minutes. This will insure complete incineration of the filter and the reoxidation of any ferrous oxide that may have been formed, which will be much easier and more complete if macerated paper has been added before the final precipitation. As the last portions of water are not always completely expelled by the heat of a Bunsen or Meker burner, it is best to blast for ten minutes,[1] the crucible being vertical and covered, and the flame playing only on the bottom of the crucible.

After cooling in the desiccator, the crucible is weighed,[2] and the difference between this and the weight of the empty crucible, obtained prior to the ignition of the silica (p. 143), is that of the Al_2O_3, total iron as Fe_2O_3, Mn_3O_4, TiO_2, ZrO_2, P_2O_5 and a trace of SiO_2. This may be noted as $Al_2O_3+Fe_2O_3+x$. The amounts of these various constituents are determined separately, and that

[1] Blum (Jour. Am. Chem. Soc., **38**, p. 1293, 1916) has shown that blasting for ten minutes is as effective as for half an hour.

[2] Blum (op. cit., p. 1292) has shown that even the blasted alumina is markedly hygroscopic, so that it is necessary to keep the crucible closely covered while in the desiccator and during the weighing.

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of alumina by difference. If three 11-cm. filters have been used, it is best to subtract their weight also from that of the ignited precipitate.

The ignited precipitate in the crucible is used for the determination of total iron, titanium dioxide and the trace of silica, its solution being effected by fusion with potassium pyrosulphate. This process may be advantageously begun immediately after weighing, as it takes several hours.

Fusion with Pyrosulphate.[1]—The ignited ammonia precipitate is very complex. It contains, with all rocks, all of the alumina, ferric oxide, titanium dioxide, phosphorus pentoxide, and manganous oxide if persulphate was added before the precipitation, as well as the small amount of silica that has escaped the first evaporations to dryness; and with some rocks it contains also all the chromium, vanadium, zirconia and the rare earths. If two or three solutions and reprecipitations of the ammonia precipitate have been made, it also is contaminated with the small amount of ash derived from the filter papers which may not be negligible in accurate analyses. Of these constituents only the ferric oxide (which includes the oxidized ferrous oxide of the rock), the titanium dioxide, and the silica are determined in this precipitate, the others being determined in separate portions and duly allowed for in order to arrive at the weight of the alumina.

The precipitate is best brought into solution by fusion with potassium pyrosulphate, which operation is carried out as follows:

Four or five grams of lumps or coarsely powdered potassium pyrosulphate are placed in the crucible containing the precipitate, so as to completely cover this, and care being taken to avoid mechanical loss of the precipitate. The amount used will vary somewhat with each rock, but those mentioned will usually be sufficient. In general, it is hardly necessary to weigh out the pyrosulphate, but to add enough to fill the crucible about one-third.

The crucible is placed over a low flame, and heated gently till the salt is fused. It is then raised to a distance above the flame (about 20–30 cm.), where the pyrosulphate will remain in a state of fusion and the moisture which it contains will be driven off, without any boiling or spattering against the crucible cover. With

[1] Mellor, p. 184. Hillebrand (p. 105), adopts a somewhat different method.

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some practice the height can be adjusted easily, and this point is an important one to attend to, as any drops on the cover or the upper sides tend to spread on further heating and run over the edges, leading to loss of iron. The whole process at this stage must be carefully watched to guard against this mishap.

It may happen, even if great care is taken, that there is a slight creep of the salt around the rim and about the cover. This is almost always caused by too intense or too rapid heating. This deposit should not be touched when moving the crucible to the slab or disturbed during the cooling.

In the course of half an hour or so all water will be driven off, and the crucible can be lowered gradually till it is immediately above the small flame, where it is kept for another hour or so. Here also the contents should be watched at intervals to see that there is no spattering. The precipitate has been gradually dissolving and the fused salt become darker in color. The larger lumps of oxide stay at the bottom, while some may float on the top of the liquid.

When the greater part of the floating portion has dissolved, any small particles which may be adhering to the sides above the level of the liquid may be washed down by a slight rotary motion of the crucible. The flame is then raised a little. This more intense heating should be carried out with caution to avoid boiling, and, until the last stages, the bottom of the crucible should not be allowed to become red-hot. White vapors of sulphur trioxide are given off, and the crucible is examined every now and then till all the floating precipitate has been dissolved. If any particles obstinately adhere above the liquid, the crucible may be held obliquely in the triangle, so as to let the fused salt act on these.

The heat is then increased somewhat until the bottom of the crucible is a faint red, the liquid getting thicker through loss of sulphur trioxide and the formation of the more difficultly fusible normal potassium sulphate. The liquid mass becomes also a very dark brown, almost opaque if much iron is present, the depth of color increasing with the temperature. This is due to the greater dissociation with increasing temperature, and the consequent larger proportion of yellow or brown iron ions.

The bottom of the crucible may be examined, notwithstanding the opacity of the liquid, to see if all the precipitate has been dis-

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solved, by removing the flame, and allowing the crucible to cool with the cover off. The fused mass will gradually become less opaque and lighter in color, till it is transparent enough to be seen through before solidification commences at the surface.[1]

When no more undissolved substance is visible, the heating at a low red heat is continued for half an hour, to render complete solution certain, and the crucible is placed on a stone or iron slab to cool. This cake loosens from the crucible far more readily than that of the sodium carbonate fusion, often with a ringing sound, and it also usually cracks, so that it offers no difficulty in removal.

It may seem that this process calls for almost constant attention and that it takes an inordinate amount of time. In reality, however, after one has had a little practice in adjusting the heat at the various stages, only an occasional glance is necessary, and the whole can often be accomplished in from three to four hours, especially if macerated paper has been used, so that the oxides are in the form of a powder. This, moreover, is of no great importance, as the analyst can be busy with other parts of the analysis.

When the mass is thoroughly cold, any deposit, due to creeping, both on the crucible rim and on the cover, is washed off with a very little hot water into a 250-c.c. beaker. Water is then poured into the crucible from the wash-bottle, enough to about half fill the crucible, and it is gently heated till the cake loosens, when this is transferred by means of the platinum spatula to the 250-c.c. beaker. The crucible is well washed with hot water into the same beaker, until all adhering sulphate is removed, and the cover is treated likewise. The final volume of liquid in the beaker may be about 100 c.c. About 10 c.c. of concentrated sulphuric acid are added, not only to facilitate the solution, but to prevent reversion to or precipitation of metatitanic acid, which would diminish the apparent amount of titanium dioxide determined later by the colorimetric method. The beaker is then heated over a low flame or on the water-bath till solution is complete, except for traces of silica, which is practically insoluble in the melted potassium pyrosulphate.

The contents of the beaker are filtered through a 7-cm. filter into a 250-c.c. Erlenmeyer flask, the first beaker being well rinsed

[1] This is more easy with potassium, than with sodium pyrosulphate.

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at least half a dozen times. The filter is also well washed. If the fusion has been successful, a few flakes of silica only will be found in the filter. If not it will also contain small, dark particles of undissolved oxide.

In any case, it is placed in an unweighed, small crucible, carbonized at a gentle heat, strongly ignited and weighed. A drop of dilute sulphuric acid and two or three of hydrofluoric acid are added, driven off by gentle heating, the crucible again ignited and weighed. The loss in weight represents the trace of silica, which is to be added to that of the main portion, already determined (p. 146). It will seldom amount to more than a milligram.

The residue left in the crucible, which will contain a little iron or titanium oxides, is dissolved by fusion with a small lump of acid potassium sulphate, which is quickly effected. After cooling, this is dissolved in the crucible in a little warm water containing a drop of sulphuric acid, and the solution poured into that in the 250-c.c. flask the crucible being also rinsed into this.

8. Total Iron Oxides [1]

The solution of the pyrosulphate fusion, obtained as above, is used for the determination of the total iron oxides as ferric oxide and for that of titanium dioxide. For the former the ferric sulphate is reduced to ferrous salt and titrated with permanganate; for the latter a colorimetric method is almost invariably used.

Iron and titanium are precipitated quantitatively and completely separated from aluminum and manganese by the new reagent "cupferron";[2] and titanium may be separated from iron by a method suggested by Thornton.[3] At the present time it must suffice to refer to these methods as available in certain cases.

Errors.—The most frequent and most serious error involved in the iron determination is incomplete reduction of the ferric oxide. This can be guarded against by allowing the gas, whether hydrogen sulphide or sulphur dioxide, to pass for a longer time than

[1] Classen, **2**, pp. 454–455; Gooch, pp. 141–146; Hillebrand, pp. 107–109; Mellor, pp. 451–453; Treadwell, **2**, pp. 607–610.

[2] Cf. Treadwell, **2**, pp. 838-842.

[3] W. M. Thornton, Jr., Am. Jour. Sci., **37**, p. 173, 1914, and ditto, **37**, p. 407, 1914.

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that which experience has shown to be generally necessary and by not boiling down to a small bulk. It can also be prevented by testing the solution for the presence of ferric salt when reduction is assumed to be complete.

A second source of error is deterioration in the strength of the permanganate solution, which can be avoided by keeping it under proper conditions and frequently standardizing it (p. 52). These precautions are often not sufficiently observed.

Zinc is not recommended as a reducing agent,[1] partly because perfectly pure and iron-free zinc is very difficult to procure, partly because of the difficulty in ascertaining when reduction is complete, partly because I do not consider that it offers any noteworthy advantage over the method adopted here, but above all because of the reducing effect of nascent hydrogen on titanic sulphate, which is always present, and on platinic and vanadic salts. The lower oxides of all three would affect the permanganate and thus appear as ferric oxide. With many rocks the amount of titanium present is so high that this would be a serious error.

With proper precautions, errors involved during the titration, such as oxidation by atmospheric oxygen, are negligible.

Reduction of Ferric to Ferrous Oxide.—The filtered solution of the mixed sulphates contains all the iron in the ferric state. This has to be reduced to ferrous for titration with potassium permanganate, to determine the total iron oxide.

As has been noted, the use of zinc for this purpose is not to be recommended, and the best reagent is hydrogen sulphide. This commends itself on account of its certainty and rapidity of action, its easy and complete removability, and still more by the fact that it has no reducing action on the titanic and platinic sulphates that are always present. Sulphur dioxide is often recommended [2] and employed, but is not so suitable for rock analysis because of its action on the platinum taken up from the crucible and basin. This is reduced to the platinous condition by sulphur dioxide, while

[1] Mellor (p. 187) advocates its use, an opinion in which I differ with him. If it be used, Gooch and Newton (Am. Jour. Sci., **23**, p. 365, 1907) recommend the use of cupric sulphate to oxidize the titanium after reduction by zinc. This, however, does not remove other objections to the zinc reduction method.

[2] Mellor (p. 191) recommends ammonium bisulphite, but this salt is not very stable on keeping and offers no special advantage over the gas.

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it is precipitated by hydrogen sulphide and can thus be eliminated. The error so involved in the use of sulphur dioxide will, of course, not be great, but may as well be avoided. Hydrogen sulphide is much more readily obtainable than sulphur dioxide—a minor, but practically important, consideration.

A current of hydrogen sulphide, washed with water, in the usual manner, is allowed to bubble at the rate of a bubble a second, through the solution in the 250-c.c. beaker, which is covered with a 4-inch watch-glass, the gas being introduced through a bent glass tube, passing through the lip and reaching to the bottom. Although Hillebrand recommends that the solution be hot, I have not found this necessary, and pass the gas through the cold solution. The current is continued till reduction is complete, which is indicated by the turbid liquid becoming clear and masses of sulphur coagulating, which are stained brown by traces of platinum sulphide, derived from the basin and crucibles. At least twenty minutes should be allowed for this, as, if the reduction is incomplete, the amount of total iron will be too low, and that of alumina too high.[1]

The glass tube through which the gas has been introduced is rinsed off into the flask, and the contents are filtered off through a 7-cm. filter into a 400-c.c. Erlenmeyer flask. This is to be done as quickly as possible, and the filter kept full. The washing is carried out with water containing some H_2S,[2] six or eight rinsings of the smaller flask and passage through the filter being sufficient. Owing to the presence of finely divided sulphur, the filtrate always becomes opalescent. But this need cause no concern, as the sulphur is completely oxidized in the subsequent boiling, by the sulphuric acid present, whereupon the liquid becomes perfectly clear.

The solution of the small cake of fused sulphate containing the residue from the trace of silica is poured in if it has not been added before, and the crucible is washed once or twice, the excess of H_2S present being more than sufficient for the complete reduction of the ferric sulphate which it contains.

If sulphur dioxide be used, the gas should be washed through

[1] The time needed will, of course, vary with the amount of iron oxide in the rock. One half-hour is usually ample.

[2] This is conveniently made in a 150-c.c. beaker after the reduction is finished.

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a small volume of water, and the acid solution should be previously nearly neutralized, by dropping in slowly a concentrated solution of sodium carbonate. This is another disadvantage in the use of this gas, as it complicates the determination of titanium by adding to the amount of alkali sulphate present.

It will now be best to test the liquid to ascertain if reduction is complete. This may be done by taking out a drop at the end of a stirring-rod and adding it to a few drops of potassium thiocyanate solution in a watch-glass resting on a white porcelain plate. If a red color appears, hydrogen sulphide should be passed through the liquid in the 400-c.c. flask for another fifteen minutes. It will not be necessary to filter after this.

Four or five small pieces of platinum foil, bent at right angles, or small pieces of a broken porcelain crucible, are then dropped in, so as to prevent bumping on boiling.

The flask is then placed over a flame, and a carbon-dioxide generator set in action, the gas being freed from possible H_2S (due to sulphides in the marble) by passing through a column of pumice soaked in copper sulphate solution, and washed by a wash-bottle containing water. The carbon dioxide is allowed to bubble at the rate of several bubbles a second, and is passed through the liquid by a bent piece of glass tubing. Complete saturation by H_2S is shown by small bubbles of this gas rising in the liquid soon after the heating begins, and long before it has become hot enough to simmer or boil.

The flow of carbon dioxide is still kept up after boiling has begun, and the boiling continued briskly until the expulsion of hydrogen sulphide is complete, as shown by occasional testing of the issuing steam with filter paper dipped in lead acetate solution. This process will take about twenty minutes, unless much opalescent sulphur is present, when possibly half an hour will be needed to clear the liquid. There is no danger of reoxidation of the ferrous sulphate, since at first the liquid contains hydrogen sulphide, and later the boiling is carried on in an atmosphere of steam and carbon dioxide.

The boiling off of the reducing gas should not be carried so far as to diminish the liquid to less than one-half of its original volume, as hot, strong sulphuric acid solution has an oxidizing effect on ferrous salts.

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The flame is now extinguished, and the flask grasped by the neck with a towel. While the stream of carbon dioxide is still passing into the flask, it is placed in a capacious vessel, such as a basin or large casserole, that is set near at hand. The contents are cooled in this, either with a stream of running water, or more conveniently and quickly by surrounding the lower part of the flask with cracked ice. The stream of carbon dioxide is continued during the cooling.

If sulphur dioxide has been used for reduction, 10 c.c. of dilute (1 : 1) sulphuric acid are to be added. This will not be necessary if hydrogen sulphide has been used.

Titration of Iron.[1]—While the liquid in the Erlenmeyer flask is cooling in a stream of carbon dioxide, the preparations may be made for the titration. The stock bottle of permanganate is shaken, so as to wash down any drops of water that have distilled onto the upper part of the bottle, and a weight burette is nearly filled with the solution, which is to be transferred with a 50-c.c. pipette, and not poured out, as this would possibly disturb the titer. If the rock is known to contain but little iron, as with a granite, a trachyte, or a rhyolite, a burette of 50-c.c. capacity will answer; otherwise one of 100-c.c. is to be taken, and this is always safer. The burette is weighed, but only to the nearest centigram, as this corresponds to one-hundredth of a cubic centimeter, less than one drop, and so is exact enough (cf. p. 35). The burette is then placed in a clamp, secured firmly, and is raised to a height that will just permit slipping the Erlenmeyer flask beneath its tip. The cap that guards the tip is removed, and the stopper turned so that the small perforations in it and in the neck coincide.

If an ordinary Mohr's burette is used, it is made ready as usual, the meniscus being brought to the zero line.

When the contents of the flask are quite cold it is placed on a white porcelain plate,[2] its mouth, just below the tip of the burette, and the permanganate is dropped slowly into the liquid, not run-

[1] For a description of the operation of titration, see page 105.

[2] In moving the flask the hand may be placed over its mouth so as to keep the carbon dioxide atmosphere in it. The gas inlet tube may be left in or, if removed, is slightly washed off both inside and outside, the washings falling into the flask.

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ning down the sides of the flask. The flask is given a rotary motion with the left hand, so as to distribute the permanganate and lessen the chance of splashing. If any drops fall or are splashed on the sides or neck they are washed down into the flask with cold, boiled water. With a little practice the proper manipulation is easily learned and the titration quickly carried out.

When the amount of standard solution needed is roughly known, about half of this may be added quickly in portions of 1 or 2 c.c. at a time, with rotation to disappearance of the color after each addition. Beyond this, the permanganate should be added by drops, with constant rotation to avoid overruning the mark. When the color begins to disappear slowly, single drops are to be added with great caution, till one of them produces a pink blush throughout the liquid which does not vanish on stirring or rotating for a short time. As very dilute solutions of permanganate are unstable, this color will vanish on long standing, even when the reaction is complete. After waiting a few moments after the addition of the last drop, the burette is wiped off and again weighed.

The number of grams of permanganate solution used is then multiplied by the amount of Fe_2O_3 equivalent to 1 gram of the standard,[1] the product giving the total iron in the rock determined as Fe_2O_3. From this is to be deducted later the iron present as FeO, and that which may exist as FeS_2.

After titration of the iron, if the amount of TiO_2 is less than 2 per cent, the solution is to be evaporated on the water-bath down to about 150 c.c. either in porcelain or platinum, the flask being rinsed well and the rinsings added during the evaporation. This liquid is to be placed in a 250-c.c. measuring flask, with glass stopper, but not filled to the mark, and reserved for the determination of titanium dioxide.

9. Titanium Dioxide

For the determination of titanium dioxide the whole volume of solution in which the total iron has been titrated is best adapted. This contains all of the titanium in solution as sulphate, and with

[1] If an ordinary burette has been used, cubic centimeters are to be understood here instead of grams.

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no possible traces of hydrofluoric acid, which exerts such a deleterious effect on the colorimetric method. If, for any reason, this solution is not available, the titanium dioxide can be determined in separate portion of rock powder, one gram of which is brought into solution by evaporation (under the hood), in a platinum crucible with a mixture of dilute sulphuric acid (1 : 1) and hydrofluoric acid. This is continued till fumes of sulphuric acid are given off, but not to dryness, when more of the dilute sulphuric acid is added, and the evaporation is continued till there are no traces of hydrofluoric acid, which may take four or five repetitions and additions of sulphuric acid. Or the solution in which ferrous oxide has been determined will answer, if it is evaporated down (in platinum) repeatedly with sulphuric acid, to expel hydrofluoric acid completely.

There are two very different methods—colorimetric and gravimetric—by which titanium dioxide is determined in rocks. The former is, by far, the most accurate and most expeditious, is best adapted to the small quantities of this constituent that are usually present in rocks, and is the method which is used by the chemists of the U. S. Geological Survey and that which I also use. It will, therefore, be described first in detail, while the gravimetric methods will be taken up later, as they are useful when the amount of titanium is very high, and all analysts may not have at hand the appliances necessary for the colorimetric method.

Colorimetric Method.[1]—This method, which was suggested by Weller, depends on the yellow to orange coloration of titanium solutions produced by hydrogen peroxide, the depth of color being proportional to the amount of TiO_2.

Errors.—In the colorimetric method for titanium there are few sources of serious error, though some corrections may have to be applied.

Vanadium, molybdenum, and chromium interfere, the first two because of the similar coloration of their solutions by hydrogen peroxide, and the last because of the normal color of the chromates. It is very seldom, however, that any of these elements is present in rocks in sufficient amount to affect the determination seriously.

[1] Classen, **1**, pp. 776–778; Hillebrand, pp. 128–134; Mellor, pp. 85–86, 203–206; Treadwell, **2**, pp. 100–102; H. E. Merwin, Am. Jour. Sci., **28**, pp. 119–125, 1909.

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Hillebrand has shown that even very small amounts of hydrofluoric acid "render this method inexact by partly bleaching the yellow color." The hydrogen peroxide must, therefore, be free from fluorine, as also must be the solution in which the titanium is determined. This bleaching effect, it may be added, has been utilized by Steiger and Merwin for the determination of fluorine (p. 235).

Strong solutions of ferric sulphate are yellowish, so that the color of this salt will be added to that of the titanium, and the result may be a somewhat serious error if the rock contains much iron. This may be corrected, as will be seen later.

Merwin [1] has shown that alkali sulphates have a very marked bleaching effect. As his standard was prepared free from alkali sulphate, there can be no doubt as to the reality of the effect. He shows, however, that the bleaching is diminished, and indeed rendered almost, if not wholly, negligible, if sufficient sulphuric acid is present.

Dunnington [2] pointed out the necessity for the presence of at least 5 per cent of sulphuric acid, but his explanation that this prevents the formation of metatitanic acid, which does not become colored by hydrogen peroxide, is probably only partially correct, as pointed out by Merwin, the solutions used by him not being strongly enough acid to prevent the bleaching effect of the alkali sulphate present.

Phosphoric acid has also a bleaching effect, but the amount of this in rocks is so small that this factor is negligible.

The eye must be practiced in the color distinctions, and the illumination must not affect the color of the solution. On this account the determination should not be made at night.

The Operation.—The preparation of the standard solution containing 0.01 gram of TiO_2 in 10 c.c. has already been described (p. 55). It will be assumed that the form of colorimeter described on p. 43 is used. If Steiger's or Schreiner's form is used, such modifications in manipulation are to be observed as are suggested in Hillebrand's description.[3]

The process is as follows: The solution of the rock in which

[1] H. E. Merwin, Am. Jour. Sci., **28**, p. 119, 1909.
[2] F. P. Dunnington, Jour. Am. Chem. Soc., **13**, p. 210, 1891.
[3] Hillebrand, pp. 35–38.

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the titanium is to be determined, and which is called the test solution, is evaporated down, if necessary, to an appropriate volume and, when cold, is placed in a stoppered measuring-flask of suitable size. The basin used for the evaporation must, of course, be washed several times into the flask. At least 10 c.c. of concentrated sulphuric acid are slowly added, and the liquid is well stirred. When it is cool 5 to 10 c.c. of hydrogen peroxide, or more than sufficient to oxidize all the titanium, is added and the liquid is diluted to the mark. It is well mixed, not by shaking, but by inverting the closely stoppered flask several times, the stopper being kept in place by the finger.

The volume to which the solution is diluted depends on the amount of titanium dioxide present in the rock. For the great majority of rocks, in which there is a little less than 1 per cent, 250 c.c. is suitable. With granites, rhyolites, and such rocks, in which the percentage of titanium dioxide is very small, a volume of 100 per cent is preferable. With rocks that contain more than 1 per cent of titanium dioxide the volume should be increased proportionately, 500 c.c. being appropriate if the percentage is about 2, and 1000 c.c. if it is about 4 or more. It is essential to have the depth of color in the test solution less, indeed, considerably less, than that of the standard solution diluted as described below.

The delicacy of this, or any other, colorimetric method is at a maximum when the color is neither very deep, nor extremely light, so that, when much titanium is present the dilution should be great. The most favorable tint is a rather deep straw-color, or about that of light beer, or clear, light amber. This corresponds almost exactly to Ridgway's "light cadmium."[1] Stated quantitatively, a favorable strength is that of a solution that contains from 0.00002 to 0.00004 gram of TiO_2 per c.c.; in other words when 10 c.c. of the diluted standard solution described below has to be diluted with from about 10 to 20 c.c. of water to bring it to the same tint as that of the test solution.

To proceed with the operation: an indeterminate quantity of the test solution is poured into one of the colorimeter glasses, say the right-hand one. Ten c.c. of the standard solution, containing about 0.01 gram of TiO_2 (the quantity being known), is removed

[1] R. Ridgway, Color Standards, Plate IV; Washington, 1912.

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from the stock bottle with a dry 10-c.c. pipette [1] and placed in a 100-c.c stoppered measuring flask Five c.c. of hydrogen peroxide are added, and the liquid is diluted with water to the mark and well mixed. Each cubic centimeter of this diluted standard will then contain 0.0001 gram of TiO_2. This amount of diluted standard will suffice for the determinations in three rocks. The color disappears after a time, so the diluted standard must be made up fresh for each determination or batch of determinations. It is evident that the color cannot be restored by addition of hydrogen dioxide to a solution already diluted to the mark, as this will increase the volume of liquid and so lessen the amount of TiO_2 per cubic centimeter. If a series of rock analyses is being made, it is well, in order to economize the standard solution, to make the titanium determinations in batches of three rocks at a time, the earlier test solutions being kept in suitable flasks, but not diluted to the mark, until the determinations are to be made.

Two burettes are fixed in a stand; the one is filled with the diluted standard, and the other with water, the position of the meniscus in each being noted. Ten c.c. of the diluted standard are then run into the left-hand glass, and water added from the other burette, in small quantities at a time. After each addition the liquid is mixed by a gentle rotary motion of the glass,[2] and the color, or rather the degree of dilution of the color, is compared with that of the test solution. In doing this the shutter should be slid down till only the liquid in each glass is visible, and none of the empty space above. As the color of the diluted standard approaches that of the test solution, the addition of water should be cautious and by a few drops at a time, till the point of agreement is reached, when the amount of water added is read off and noted down. The liquid is rejected.

Ten c.c. of the diluted standard are then again run into the again empty left-hand glass and water is added as before, the water burette being refilled if it is necessary. This procedure is repeated a third time, so that there is obtained a mean of three determinations, which should not vary more than within 1 c.c.

[1] The solution should not be poured out, and the bottle is to be closed as soon as the portion is removed.

[2] A glass rod flattened at one end (Hillebrand) may be used but there is danger of breaking the glass.

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In adding the water the second and third times it is well to cover the burette with a roll of paper held in place by an elastic band, so as to avoid any bias produced by a knowledge of the amount of water that is to be added to make the second and third observations agree with the first.

While observing the color after each addition of water, the box is held in the hand with the ground-glass end pointed toward a good, natural light, that of light clouds, if possible, or the window. The disturbing effect of sunlit foliage or brick walls is to be avoided, and, if necessary, a towel is pinned against the window so as to furnish a white screen.

The operation should be carried out in the day time, best on a bright day, as the shades of color are much more readily distinguishable by daylight than by artificial light. It will be found advantageous to rest the eyes occasionally by looking at the floor or at a dark corner, as their sensitiveness is apt to diminish with fatigue.

When testing the method with known amounts of TiO_2 for the first few times I noticed a tendency to judge that the colors matched some time before they actually should have done so. Any such tendency, or the reverse, which may be true of others,[1] is to be guarded against; to do this one must have practice with known amounts of titanium. This may be obtained by making up test solutions from small measured volumes of standard solution diluted with varying known volumes of water, and determining the TiO_2 in them. As the amount of TiO_2 is known, one has a check on the personal equation, and will soon be in a position to determine unknown quantities of TiO_2. For one who has never used the method, this preliminary practice should not be omitted. After a little practice one soon becomes able to judge of exact agreement in color and to arrive at concordant and correct results.

The principle underlying the simple calculation that is needed to determine the percentage of titanium dioxide is that, as the colors in the two solutions are identical, the amount of TiO_2 per cubic centimeter is the same in both. An example, taken from the analysis presented on p. 242, is given here, so that the principle and the calculations may be clearly understood. They

[1] Mellor, pp. 85–86, Merwin, Am. Jour. Sci., **28**, p. 120, 1909.

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apply as well to the colorimetric determinations of manganese and chromium.

The portion of rock powder taken for the main fusion weighed 1.0197 gram. The test solution, after the determination of total iron oxides, was made up to 500 c.c. It was found that 12.11 c.c.[1] of water had to be added to 10 c.c. of tenth diluted standard, which contained 0.0074 gram[2] of TiO_2 per cubic centimeter, to make its color match that of the test solution. We now have to divide 0.00074 (the weight of TiO_2 in 1 c.c. of the diluted standard) by $10+12.11=22.11$ (the volume of identically colored standard) to obtain the weight of TiO_2 per cubic centimeter. The result is 0.000033469 gram. This multiplied by 500 (the volume of the test solution) gives 0.0167345 gram as the amount of TiO_2 in the rock. Divided by 1.0197 this gives 1.64 as the percentage of TiO_2 in the rock.

A correction for the disturbing effect of high iron may be made by allowing for this on the basis of Hillebrand's[3] tests, that "go to show that the coloring effect of 0.1 gram Fe_2O_3 in 100 c.c. of 5 per cent sulphuric acid solution is about equal to 0.2 milligram of TiO_2 in 100 c.c. when oxidized by hydrogen peroxide. This amounts to a correction of only 0.02 per cent on 1 gram of rock containing the unusual amount of 10 per cent Fe_2O_3." As phosphoric acid bleaches ferric sulphate solutions as well as those of oxidized titanium, it can be used to equalize the bleaching in the test and standard solutions by adding a known amount of phosphoric acid or a soluble phosphate to each. As this will rarely be called for, the student would best consult Hillebrand (just cited) for the details.

In regard to the correction for the effect of alkali sulphates I cannot do better than quote Merwin[4] verbatim.

"In rock analysis by using 6 grams of pyrosulphate, which is equivalent to 4 grams of normal sulphate and 2 grams of acid,

[1] This is the mean of 11.8, 12.5, and 12.1 c.c.

[2] Some titanium oxide had precipitated on standing, and the solution had been filtered and restandardized by determining gravimetrically the amount of TiO_2 per cubic centimeter (p. 55). It will be clear that the standard does not need to contain exactly 0.01 gram TiO_2 per cubic centimeter.

[3] Hillebrand, Bull. 422, p. 133.

[4] H. E Merwin, Am. Jour. Sci., **28**, p. 122, 1909.

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for the melt containing the titanium, and dissolving this in water to which 10 c.c. of strong sulphuric acid has been added, a nearly negligible correction of only 3 per cent (of the TiO_2) need be added. If the TiO_2 exceeds .02 gram no correction is required (as the color is so intense that the bleaching effect will not be noticeable). In case the melt is dissolved in 100 c.c. of 5 per cent sulphuric acid, the titanium found—if the amount is between .002 gram and .01 gram—is too low by approximately .0004 gram." It will be seen that for most work the correction is negligible if the solution is made very strongly acid.

If the glasses described above are not available, and it is desired to use Nessler tubes, the method is modified as follows, according to the plan of Prof. Penfield. A light box is used of such dimensions as to snugly hold the two tubes side by side. These rest either on a ground-glass plate forming a false bottom, or on a horizontal wooden partition with holes or a broad slot cut so as to admit light from below. Beneath this or the ground-glass plate a mirror is fixed at an angle of 45° above the real bottom, admitting light from a side-opening and transmitting it vertically up through the tubes.

The test solution is prepared as above, but the standard is used undiluted. One Nessler tube is filled with the colored test solution up to the 50-c.c. mark, and in the other is placed 5 c.c. of hydrogen peroxide, which is diluted with a known volume of water nearly up to the same mark. The standard solution is then added in very small quantities at a time from a burette, the liquid being stirred, and the colors observed after each addition, till there is agreement between the two. After a few trials, and with knowledge of the approximate amount of titanium present in the rock, the heights of the two solutions can be made sensibly identical, but several determinations are always advisable. The Nessler tube for the standard solution is to be emptied and washed carefully each time.

While this modification involves the use of more easily obtainable glass vessels, as well as less standard solution, it is not quite as accurate as the other, although sufficiently so for many purposes, and is far more so than the gravimetric method sometimes used.

Another alternative apparatus is that of Schreiner, described

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by Hillebrand.[1] This consists essentially of two graduated glass tubes to hold the test and diluted standard solutions, the liquids being examined vertically. The depths of the two columns of liquid are changed by means of two smaller glass tubes with flat bottoms immersed in them, the graduated tubes being moved up or down until the shades are identical. The strengths of the two solutions are inversely as the heights of the columns. This apparatus is said to give good results. A new form of colorimeter which has recently been described by G. Steiger[2] utilizes the same principle. It is the form which is now used in the Survey laboratory.

Gravimetric Methods.—Although the colorimetric method for the determination of titanium is by far the simplest and most expeditious, is capable of adequate accuracy, and is applicable in the great majority of rocks, it is not so well suited to rocks or minerals which contain more than about 5 per cent of TiO_2, because of the loss in delicacy with great depth of color, and the possibility of serious error with the large dilution necessary to overcome this. Occasion may therefore arise for the determination of titanium by gravimetric methods. Although the use of these is not recommended, if the colorimetric method is applicable, some of the recent and more accurate methods may be described briefly.

One of the best gravimetric methods is that of Gooch,[3] which is fully described by Hillebrand,[4] to whom the student may be referred. Although it is rather complicated, it is satisfactorily accurate for most rocks. Hillebrand has shown that it is not to be used when zirconia is present, but as large amounts of these two oxides rarely occur together in the same rock, this consideration is of very slight practical importance.

A simplified modification of this method, due to Prof. H. Fay, is described by Warren,[5] who states that it is "highly satisfactory, both in point of simplicity and accuracy." His description of it is quoted here.

"Fuse 0.4–0.6 gram of finely ground ore with 6–8 times

[1] Hillebrand, p. 37.
[2] Ibid., p. 35.
[3] F. A. Gooch, U. S. Geol. Surv., Bull. 27, p. 16, 1886.
[4] Hillebrand, p. 134.
[5] C. H. Warren, Am. Jour. Sci., 25, p. 23, 1908.

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its weight of mixed alkali carbonates until action ceases. Extract the mass with hot water, and decant the solution through a filter. Boil the residue with 25 c.c. of sodium carbonate solution, filter and then wash the residue on the filter paper several times with dilute sodium carbonate solution. Place the filter and residue in a platinum crucible and ignite at a low temperature until the filter paper is burned. Fuse with 12–15 parts (5–9 grams) of dry acid potassium sulphate for one-half hour. The temperature of the fusion should be so regulated that the mass is kept in the molten condition, but sulphur trioxide should escape only when the lid of the crucible is removed. Cool and remove the fusion from the crucible by means of a long platinum wire, which has been inserted in the fused mass. Suspend the fusion in 200 c.c. of cold water to which has been added 100 c.c. of sulphurous acid and allow to stand in a cool place until solution is complete.

"Filter if necessary. To the solution add 125 c.c. acetic acid (sp.gr. 1.04) and dilute to 800 c.c. in a liter beaker. Add 20 grams of sodium acetate dissolved in a small amount of water and boil from 3–5 minutes, adding *just before the boiling-point is reached* an additional 25 c.c. of sulphurous acid. Allow to stand in a warm place for one-half hour and then filter by means of a siphon through a 9-cm. paper.

"Wash the precipitate with 5 per cent acetic acid solution until most of the sulphate has been removed, and then ignite the paper and precipitate. Fuse with acid potassium sulphate again. Proceed exactly as before, finally igniting and weighing the precipitate as TiO_2."

Warren states that in two determinations 0.01 per cent of iron could be detected in the precipitate and that probably the same amount of alumina and manganese are included. For very accurate work a third precipitation is advisable. In a letter he lays stress on the importance of adding the additional 25 c.c. of SO_2 just before the boiling begins.

Another modification of Gooch's method has been worked out by Thornton [1] in analyzing some rocks that are exceptionally high in iron and titanium. It depends on the reduction of the iron in presence of tartaric acid (to hold up the titanium) and precipita-

[1] W. M. Thornton, Jr., Am. Jour. Sci., 34, pp. 173, 214, 1912.

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tion of the iron as sulphide. After oxidation and destruction of the tartaric acid, by the action of sulphuric and nitric acids, the titanium is determined by the basic acetate method. The published results are very satisfactory.

As I have tried neither of these methods, they can but be suggested to the student for use in case of need.

Thornton has also [1] devised a method for the separation of titanium from iron, aluminum, and phosphoric acid by the use of "cupferron." This method seems to be promising, and if the reagent needed becomes readily procurable, will probably be worthy of trial in special cases.

The method of precipitating metatitanic acid by prolonged boiling of a very dilute sulphuric acid solution in the presence of sulphur dioxide should not be used, as this antiquated method is very unreliable. Precipitation of metatitanic acid is by no means complete in all cases, and that which is precipitated is almost always contaminated by alumina and ferric oxide. It is also extremely liable to adhere very firmly to the sides of the beaker, from which it is removed with great difficulty. It is as apt to give too high as too low results, and, after thorough trial, with various modifications, I have rejected this method entirely.

10. Lime [2] (and Strontia)

For the determination of lime the filtrate from the ammonia precipitations is used (p. 157); or if manganese has been determined as sulphide (p. 224), the filtrate from this may be used, in which case the ammonium sulphide need not be destroyed. The volume of liquid should not amount to more than about 500 c.c., and is contained in an 800-c.c. beaker. If it is more than this it is advisable to evaporate it down (in a porcelain or platinum basin) to 400 c.c. This should not be necessary if care has been taken to avoid unduly large quantities of wash water. If a precipitate (of calcium carbonate) forms it is dissolved with a little acid.

Errors.—There are very few possible errors involved in the

[1] W. M. Thornton, Jr., Am. Jour. Sci., **37**, p. 407, 1914.

[2] Classen, **1**, p. 794; Fresenius, **1**, pp. 270–272; Gooch, pp. 86–88; Hillebrand, pp. 118–119; Mellor, pp. 211–214; Morse, pp. 430–431; Treadwell, **2**, pp. 70–71.

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determination of lime; indeed, as has been said already, this constituent and silica are those which are most likely to be approximately correct in second-rate work.

The error caused by the presence of carbonate in the ammonia water has been mentioned on p. 148, in connection with the determination of alumina. This, of course, would render the apparent amount of lime too low, but it can be prevented very easily by testing the ammonia water with calcium or barium chloride. The magnitude of this error will never be very great, unless grossly impure or very old ammonia water is used.

The first precipitate of calcium oxalate invariably contains some magnesia and soda, so that solution and reprecipitation are always called for. The oxalate should be ignited to oxide, never weighed as carbonate or sulphate, and the oxide should be ignited to constant weight, at least until experience has taught the time necessary for the ignition. Blasting is not necessary.

Precipitation.—About 25 c.c. of ammonia water (previously tested for carbonate) is added, and I have found it useful also to add 50 c.c. of alcohol. The liquid is stirred and heated to boiling. During the heating 1-3 grams of ammonium oxalate, according to the amount of lime in the rock, are dissolved in 25 c.c. of water with the aid of heat. This solution is poured into the large beaker when the liquid in it begins to boil and the whole is well stirred. The boiling is continued for a few minutes, and the liquid is allowed to stand for two or three hours, or better for six, or over night, if there is but little lime.

The liquid is filtered, after standing, through a 7- or 9-cm. filter, according to the amount of lime, the filtration and first washing being carried out as described above (p. 92). The filtrate is received in an 800-c.c. beaker, and when this becomes rather more than half full, another 800-c.c. beaker is substituted for it. This is rather more convenient than using one 1000-c.c. beaker.

After slight washing, the precipitate in the filter is dissolved and washed into the original 800-c.c. beaker as has been described (p. 94), a few cubic centimeters of ammonium oxalate solution are added to the filtrate, the liquid is heated nearly to boiling, and the lime reprecipitated by the addition of sufficient ammonia water to give a strong ammoniacal odor. A little alcohol may also be added.

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After standing for several hours the precipitate is filtered off, the filtrate passing into the second 800-c.c. beaker. The calcium oxalate is washed well, but not over-washed, some drops of the ammonium oxalate solution being added with each addition of wash water. A second reprecipitation is not called for.

The precipitate is ignited moist as already described (p. 102). The calcium oxide is ignited over a Meker burner for thirty minutes, which will be sufficient to change the oxalate completely to oxide in most rocks. If much lime be present it is well to ignite again, after weighing, until the weight is constant. The calcium oxide should be kept covered in the desiccator, and weighed as rapidly as possible, with the crucible covered. Its weight is divided by that of the rock powder taken, in order to get the percentage of CaO.

Strontia.—The calcium oxide, as obtained above, contains all the strontia of the rock, but scarcely ever more than traces of the baryta. The amount of strontia is always very small, not more than 1 milligram or less, except in a very few, highly unusual rocks. In most analyses, therefore, it need not be determined, especially as it enters rock minerals as an isomorphous replacer of lime. It will be well, however, to determine it in some rocks, as in one or two of a series, since we know little of its relationships to the other constituents. There are no serious errors involved.

The method that is recommended is based on the solubility of calcium nitrate in a mixture of ether and absolute alcohol, and the insolubility of strontium nitrate in this medium.[1]

After the lime has been finally weighed, and before it has absorbed any appreciable amount of carbon dioxide from the air, it is slightly more than moistened with a few drops of water in the crucible in which it was weighed. Nitric acid is added, drop by drop, until the lime is just dissolved. The contents of the crucible are evaporated to complete dryness on the water-bath, and when cold about 5 c.c. of a mixture of absolute alcohol and ether is poured in. The crucible is tightly closed with a well-fitting cork, and laid aside in a cool place for at least twenty-four hours.

The contents of the crucible are then to be filtered through a 5½-cm. filter and well washed (six times) with the same mixture of

[1] Classen, **1**, p. 797; Fresenius, **1**, p. 621; Hillebrand, pp. 119–120; Mellor, pp. 514–515; Treadwell, **2**, pp. 78–80.

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absolute alcohol and ether. The filter is allowed to dry in the funnel, after which the strontium nitrate is dissolved in a few cubic centimeters of water passed through the filter and received in a 50-c.c. beaker, the filter being washed a few times. A few drops of dilute sulphuric acid are added and then alcohol equal in amount to the volume of liquid in the beaker. After standing for twelve to twenty-four hours the precipitated strontium sulphate is filtered off, ignited and weighed. Its weight is multiplied by .56 to obtain that of SrO, and this is deducted from that of the lime.

11. Magnesia [1]

The filtrate from the calcium oxalate contains, of the original rock constituents, only the magnesia and alkalies, with the barium, and part of the manganese and the nickel and other metals of the sulphide group, if these have not been previously separated. There are, of course, also present the alkalies derived from the carbonate fusion and large amounts of ammonium salts. It will not be necessary to remove these last for the determination of the magnesia, which is the only constituent that interests us in this filtrate.

Errors.—The chief source of error in the determination of magnesia is that already mentioned in connection with alumina, namely, the tendency to partial precipitation by ammonia along with alumina. This must be prevented by the presence of sufficient ammonium salts and repeated precipitations, as already described.

An error of less magnitude and importance, but which should be avoided, is that involved in the precipitation of the ammonium-magnesium phosphate. If there be present excess of ammonia, ammonium salts and precipitant, the ammonium-magnesium phosphate, and hence the magnesium pyrophosphate, will not be normal in composition, owing to the presence of extra P_2O_5, as pointed out by Neubauer [2] and by Gooch and Austin.[3] This must

[1] Classen, **1**, pp. 830–834; Fresenius, **1**, pp. 275–276; Gooch, pp. 81–84; Hillebrand, pp. 123–126; Mellor, pp. 215–221; Ostwald, pp. 149–151; Stieglitz, p. 165; Treadwell, **2**, pp. 65–67.

[2] Neubauer, Z. Angew. Chem., 1896, p. 435.

[3] Gooch and Austin, Am. Jour. Sci., 7, p. 187, 1899.

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be corrected by solution of the first precipitate and reprecipitation from the acid solution by a slight excess of ammonia. This error will not affect the other constituents, but will raise the figures for MgO only, and hence the summation of the analysis will be too high. The error due to this cause will usually be of slight magnitude and seldom of the importance attributed to it by Robinson.[1]

The magnesia will be low if the precipitate of calcium oxalate is not dissolved and reprecipitated.

A marked loss has been shown by Connor[2] to take place on evaporation of the magnesium pyrophosphate with nitric acid, as is often done to free it from adherent traces of carbon.

The figure for magnesia will also be slightly high, if manganese has not been separated previously. For most rocks this error is quite negligible.

Precipitation.—The total filtrate containing all the magnesia now amounts to some 800 c.c. or more, contained in two 800-c.c. beakers. To each is added 100 c.c. of ammonia water and about 50 c.c. of alcohol. A solution is made of about 3 grams of sodium-ammonium phosphate in 50 c.c. of hot water and, after stirring, this is divided between the two beakers. The precipitation is made in the cold, not in a hot solution. The mixture in each beaker is to be well stirred, taking the precaution not to let the stirring-rod touch the sides, and the beakers are laid aside (covered) for at least twelve, and preferably twenty-four hours.

At the end of this time the liquid is filtered and the beaker and the precipitate are washed slightly with water containing about 5 per cent of ammonia water, the filtrate being rejected. The precipitate in the filter is then dissolved in about 25 c.c. of warm, dilute nitric acid (1 : 5), the solution being caught in one of the two 800-c.c. beakers. The precipitate adhering to the sides of both is also washed down and dissolved in dilute nitric acid, which is passed through the filter, and the beakers and filter are well washed. All this is carried out as described on pp. 91–98.

At the end, the nitric acid solution, which will be in but one of the beakers and should amount to not more than 150–200 c.c., will contain all the magnesia. About one-third of this volume of ammonia water is added, as well as a little alcohol, and one or two

[1] H. H. Robinson, Am. Jour. Sci., **41**, p. 260, 1916.
[2] M. F. Connor, **12** Cong. Geol. Int., C. R., p. 886, 1914.

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drops of the phosphate solution, the liquid is stirred, and again allowed to stand. Three or four hours of standing will be sufficient.

The final precipitate may be collected in either a Gooch crucible or a paper filter. The former is rather the better, on the whole, though it makes little difference which is used. If a Gooch crucible is used, this is prepared and the filtration and ignition are carried out, as described on pp. 99–101. If paper is used the precipitate is collected on the same filter that has been used before, a little weak ammonia being passed through it first. As the fine precipitate has a tendency to creep up the glass wall of the funnel, this should be guarded against. The ignition in the moist paper is carried out as with the silica, except that the paper should be carbonized and burnt away more slowly.

In either case the precipitate is ignited over a Meker burner for twenty minutes or more, and brought to constant weight. Blasting is not generally necessary.

After cooling in the desiccator the crucible and its contents are weighed, the gain in weight being $Mg_2P_2O_7$. This is to be multiplied by the factor 0.3621 to reduce it to MgO.

Beginners will do well to test the completeness of the separation of magnesia and alumina by examining the solution in which TiO_2 has been determined (p. 169). Alumina and iron are to be precipitated by ammonia in the whole, or an aliquot part of this solution. The precipitate is filtered off, and magnesia, if present, is determined by the method just described.

12. Ferrous Oxide [1]

Ferrous oxide is determined in a separate portion of rock powder. For rocks, such as granites or rhyolites, that contain but little of this constituent, it is well to use 1 gram; but for most rocks ½ gram will be an appropriate amount.

Several methods of different kinds have been proposed, and will be found mentioned by the authorities just cited. Of these, that of Mitscherlich [2] has been frequently used, especially in Europe. It consists in decomposing the rock powder with dilute

[1] Classen, **2**, pp. 620–623; Hillebrand, pp. 154–171; Mellor, pp. 461–466; Treadwell, **2**, pp. 502–504.

[2] For a discussion of this method see Hillebrand, p. 157.

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sulphuric acid in a sealed glass tube under pressure. This method is open to many objections: liability of the glass to be attacked; difficulty of ascertaining when decomposition is complete; the insuring of an oxygen-free atmosphere; the inaccuracy of the method if sulphides are present; and the great trouble and time involved in the procedure. The Mitscherlich method will, therefore, not be considered further.

There are several modifications of the method of decomposing the rock powder by a mixture of sulphuric and hydrofluoric acids in a non-oxidizing atmosphere. Of these those of Cooke and of Treadwell are often recommended, but as they demand somewhat elaborate apparatus, do not readily insure complete decomposition, and take much time, they also will not be described here.[1]

The only method that will be dealt with here is Pratt's simplified modification,[2] which has been used for years and found to give concordant and satisfactory results.

Errors.—The correct determination of ferrous oxide has long been one of the most difficult and uncertain points in the analysis of rocks. The chief difficulty, of course, lies in the solution of the material without oxidation of the ferrous oxide to ferric.

It was formerly thought to be imperative that, whatever the method employed for the determination of ferrous oxide, the rock powder should be in an extremely fine state of division, and the use of a specially ground powder was previously advocated by Hillebrand and also by myself in the first edition of this book.

Mauzelius[3] has, however, shown that there is a decided tendency to oxidation of the ferrous iron during grinding, and that this becomes the more marked the longer the grinding and the finer the powder, so that he recommends the use of as coarse a powder as will be completely attacked by the acid. These conclusions have been confirmed, in the main, by Hillebrand,[4] who attributes the oxidation to strong local heating at the moment of fracture of the grains under the pestle. The oxidation can be diminished or

[1] Descriptions will be found in the works cited above.

[2] J. H. Pratt, Am. Jour. Sci., **48**, p. 149, 1894.

[3] R. Mauzelius, Sver. Geol. Unders., Aarbog I, No. 3, 1907.

[4] Hillebrand, Jour. Am. Chem. Soc., **30**, p. 1120, 1908 and Bull. 422, p. 154; Mellor, p. 124; Treadwell, **2**, p. 837; Sosman and Hostetter, Trans. Am. Inst. Min. Eng., p. 919, 1917.

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even completely avoided by grinding under inert liquids, as water, carbon tetrachloride, or alcohol, the last being the most suitable. It must be observed, as regards Hillebrand's investigations, that the times of grinding were very long, at least two hours or more in most cases, a mechanical grinder being used and the powder being reduced to an extreme fineness. When the grinding was half an hour or less the oxidation seems in general to have been negligible.

It seems to follow from these investigations that to obtain correct results for FeO, the rock powder must be as coarse as is consistent with proper solution in the acids employed, and that long-continued grinding is to be avoided in preparing the sample. In the method adopted by me for preparing the sample (p. 68), the time spent in crushing is very short and the grinding of the final small residue lasts only five minutes or less, so that the oxidation of the resulting powder will be negligible. I have also found that such a powder is easily and completely attacked and dissolved by the Pratt method in the case of all rocks tested, ranging from rhyolites and granites to basalts. The main portion of the sample may, therefore, serve for the ferrous oxide determination without further preparation or grinding. For ordinary rock analysis the grinding of the powder under alcohol is not to be recommended, as it involves some sources of error and loss of time through drying.

On the whole, however, I must advocate the special grinding of the powder for the ferrous oxide determination because of the shorter time needed for complete decomposition. Indeed I still use it for most rocks, especially those that contain considerable ferromagnesian minerals, pyroxenes, amphiboles, and biotites, which are attacked with difficulty by the acids used. As an illustration of the data obtained in practice which have led me to the retention of this procedure, I may cite two determinations of FeO recently made on the same sample of an aegirite from Laven. The first was made without, and the second with, fine grinding; the results were, respectively, 6.85 and 6.88 per cent.[1] With such rocks as granites, rhyolites, or trachytes, that contain but little iron and are readily decomposed, the fine grinding may well be omitted.

[1] These were made without boric acid.

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There is always present the possibility of partial oxidation, both by atmospheric oxygen and by the sulphuric acid, during the decomposition, and this may be very serious. It can be guarded against and eliminated by careful manipulation, but uniform success as regards this point is only to be attained by practice and experience.

If sulphides, vanadium as V_2O_3, or organic matter are present they will reduce the permanganate and render the results too high. Organic matter is not to be generally expected in igneous rocks, and in the great majority of them sulphides and vanadium are only present (if at all) in amounts so small as to make their influence quite negligible. This point is discussed by Hillebrand,[1] who may be consulted for details. If any considerable amount of sulphides is present there would seem to be no method now known to obtain correct figures for ferrous oxide.

The presence of hydrofluoric acid in the solution is a very important factor. While solutions of ferrous oxide in dilute sulphuric acid are fairly stable, they are much less so if hydrofluoric acid be added. Furthermore in the presence of this acid the end point is transitory, and often several cubic centimeters of permanganate can be added without obtaining a permanent coloration; so that it is often difficult to finish the titration with certainty or accuracy.

Manganous sulphate is oxidizable by permanganate, so that if the rock contains much iron, the very considerable amount of manganous salt formed by the reaction of the permanganate on the ferrous oxide also renders the end-point fleeting and the titration somewhat uncertain.

Thus the presence of both hydrofluoric acid and manganous sulphate are deleterious, and as they are both necessarily present in the analysis of rocks, it is obvious that the determination of ferrous oxide in them must often be looked on with some suspicion as to its accuracy.

Several suggestions have been made to counteract these deleterious effects, that of hydrofluoric acid especially. Thus, Gage[2] proposed the addition of calcium phosphate, with the view of removing the fluorine from the solution by precipitation as cal-

[1] Hillebrand, Bull. 422, pp. 165–166.

[2] R. B. Gage, Jour. Am. Chem. Soc., 31, p. 381, 1909.

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cium fluoride. Fromme [1] converts the hydrofluoric into fluosilicic acid by the addition of silicic acid, while Dittrich [2] uses potassium sulphate and silicic acid.

The matter has recently been investigated thoroughly by Barnebey,[3] who studied the effect of a number of additions. He finds that those proposed, as well as some others, are not entirely effective or satisfactory, but that the presence of boric acid in excess renders the solution stable in presence of air, and gives a definite and lasting end-point. Indeed, the addition of boric acid would seem to have solved the problem of the exact titration of ferrous oxide in silicate rocks.

It must not be thought, however, that it is essential, as exact and concordant determinations can be made by an experienced analyst without its use. Thus Hillebrand [4] says: "It is possible to titrate ferrous iron in presence of sulphuric and as much as 5 to 7 c.c. of 40 per cent hydrofluoric acid in a total volume of 200 to 400 c.c. almost if not quite as exactly as in sulphuric acid alone, provided that the iron solution is diluted with air-free water and the titration is made immediately after adding the hydrofluoric acid and with all possible dispatch." For the beginner, however, and even for the experienced analyst, it will be well to follow Barnebey's recommendation and titrate in the presence of boric acid.

There is a decided tendency to minus errors in the determination of ferrous oxide.

Simple Method.—There are several modifications of the method of decomposition by a mixture of hydrofluoric and sulphuric acids, which differ in comparative simplicity and, to some extent also, in accuracy. The simplest, and the one which I have found to be sufficiently accurate for most purposes and by far the most rapid, will be described first. This is essentially the method first tested by Pratt, and is simpler than that now adopted by the U. S. Geological Survey. I have found it to give accurate and concordant results.

About half a gram of the rock powder [5] is weighed into a 35-c.c.

[1] J. Fromme, Tscher. Min. Pet. Mitth., **28**, p. 329, 1909.
[2] M. Dittrich, Cf. Chem. Abstr., **5**, p. 846, 1911.
[3] O. L. Barnebey, Jour. Am. Chem. Soc., **37**, p. 1481, 1915.
[4] Hillebrand, Bull. 522, p. 161.
[5] This may or may not be specially ground. See page 183.

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platinum crucible,[1] the cover of which must fit closely. It is moistened with a little water, this being blown in gently against the side of the crucible, the tip of the wash-bottle being inserted beneath the slightly raised cover. In this way the mass may be wet without blowing out any of the rock powder. When thoroughly wet and pasty a few small coils of platinum wire are dropped in, to prevent bumping. If carbonates are present in the rock, a few drops of very dilute sulphuric acid is poured in and the cover quickly put on, until effervescence ceases.

In the meantime the nearly full hot water wash-bottle is heated until the water boils vigorously so as to drive out all dissolved air; after which it is cooled under the tap.

In another platinum crucible or the small basin, about 10 c.c. of warm dilute sulphuric acid is made by slowly pouring 5 c.c. of the concentrated acid into 5 c.c. or so of the cold, boiled water. Into this is poured about 5 c.c. of hydrofluoric acid, an operation that must be done with caution and in small portions at a time. Hydrofluoric acid causes painful and lasting sores and too great caution cannot be exercised in handling it.

The crucible containing the wet rock powder is placed in a triangle resting on a ring of a retort stand in the hood. It must not be pressed into place, but laid in loosely so that it will be easily removable. The ring should be at a height so as to bring it about 10 cm. above a small Bunsen burner flame. The Bunsen burner is lighted, its flame adjusted to a height of about 2 cm. high, and is placed near by, not beneath the crucible.

The crucible is now uncovered with the left hand, enough of the warm mixture of sulphuric and hydrofluoric acids is gently but quickly poured in so as to fill the crucible about half-full, and the cover is quickly put in place, but not pressed down tight.

With the Bunsen burner waved somewhat below the crucible, the liquid is heated until it just begins to simmer, but not boil, when the flame is slowly lowered and the burner put in place below the crucible. The points to be attended to are that the hot liquid should begin to steam and so replace the air in the crucible as soon as possible, and should be kept simmering continuously, but without any bumping or foaming so as to cause loss by spattering or boiling over.

[1] A large crucible is necessary to prevent boiling over.

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This may be attained by properly adjusting the size of flame and the height of the crucible above it. These will vary, of course, with different conditions, but I have found that with a flame about 2 cm. high the 40-c.c. crucible used for this operation should be about 15 cm. above its tip. Some practice is needed but the right conditions will soon be learned. At first the crucible must be watched, and the operation proceeds properly when the liquid is heard to be simmering gently and a little white vapor issues from around the cover. The liquid must never " bump."

When all is proceeding well, or before the acid is added, a 600-c.c. beaker [1] is slightly more than half filled with the cold boiled water, about 5 or 10 c.c. of dilute (1 : 1) sulphuric acid are poured in, and (following Barnebey) 2 or 3 grams of solid boric acid are added. This beaker is placed near the heated crucible.

The simmering is continued for five to eight minutes, according as the rock is largely feldspathic or is rich in ferromagnesian minerals. For the great majority of rocks I find that six minutes is ample for complete decomposition, and yet not long enough to cause sensible oxidation of the ferrous oxide by the hot sulphuric acid. The time is best noted by one's watch laid on the bench near by.

When the allotted time is up the crucible is firmly grasped in a pair of Blair's tongs, rather above the center, and is plunged quickly but without any splashing into the water in the 600-c.c. beaker standing at hand and the tongs are immediately withdrawn. The tongs are best provided with platinum shoes, but those of German silver or brass will answer. Tongs of the ordinary form are not so well adapted for this, as they cannot grasp the covered crucible firmly without danger of slipping or letting the crucible tilt.[2]

The contents of the beaker are to be titrated with standard permanganate solution immediately after the crucible has been

[1] For very exact work the lower half of a large ceresine bottle may be used in place of a glass beaker.

[2] In default of the proper tongs the crucible may be lifted with the handle portions of two ordinary test-tube holders (the smaller piece being removed), with the ends slightly hollowed so as to fit the crucible. These are held vertically, one in each hand, and the crucible is grasped firmly on either side rather near the top. As suggested by Mellor, a loop of platinum wire may be previously fixed around the crucible extending (say about 10 cm.) above it.

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dropped in; the burette being already filled, weighed, and in place for this purpose. During the titration the liquid is gently stirred with a glass rod, and the crucible and cover are moved about so that the permanganate may reach all parts of it and the contents of the crucible be thoroughly emptied and mixed with the liquid in the beaker.

The titration is carried out to the first pink blush that persists for a few seconds in spite of stirring. After titration the contents of the beaker should be examined to see if decomposition has been complete, which will be shown by the absence of hard, gritty, or dark particles. If such are present the operation should be carried out again on another weighed portion of powder, this being ground specially fine, if it has not been before, or the heating continued for a longer time.

With rocks that contain much lime or magnesia the liquid will be somewhat turbid. This is not an indication that the decomposition is incomplete, but is due to the formation of calcium sulphate and fluorides of calcium and magnesium.

The burette is now weighed. The loss in weight (or the number of cubic centimeters if an ordinary burette is used), is multiplied by the FeO value of 1 gram (or c.c.) of the standard permanganate solution; the product, divided by the weight of rock powder taken, is the percentage of FeO. The loss in weight (or number of cubic centimeters) is also to be multiplied by the Fe_2O_3 value of 1 gram (or c.c.), to arrive at the percentage of Fe_2O_3 that corresponds to that of FeO. The weight of rock powder taken for the " main " portion, in which the total iron oxides has been determined, is multiplied by this, and the product subtracted from the weight of the total iron oxides (pp. 167, 244). The remainder is the weight of the Fe_2O_3 of the rock.

It may sometimes happen, especially with rocks rich in nephelite or minerals which gelatinize with acids, that the powder cakes at the bottom of the crucible, preventing complete decomposition. This is usually due to the powder not having been thoroughly stirred up with enough water before the addition of the mixed acids. In such a case the best remedy is to repeat the whole operation until successful, or the rock powder may be intimately mixed with powdered quartz.[1]

[1] Suggested by Dittrich; see Mellor, p. 462.

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After titration the liquid is to be poured into the sink and the beaker well washed, so as to prevent its corrosion by the hydrofluoric acid.

Pratt's Method.—The simple method described above was modified by Pratt,[1] by allowing a current of carbon dioxide to flow into the crucible during the boiling by a platinum tube passing through a hole in the cover. As modified by Hillebrand [2] the method now employed in the Survey Laboratory is as follows: The rock powder in the crucible is mixed with 10 c.c. of dilute sulphuric acid, the crucible is placed in a triangle over the burner, and the air is replaced by carbon dioxide, which enters beneath the lid slightly raised on one side. Before the liquid boils the gas current is stopped and the well-fitting lid is lowered; 5 to 7 c.c. of strong hydrofluoric acid are then quickly poured in through an opening formed by drawing the lid a trifle to one side, the lid is replaced, and the boiling continued for the requisite time. The rest of the operation is as above. This method has certain apparent advantages over the first, but I am inclined to think that there is little to choose between them, so far as accuracy is concerned.

Mellor (p. 464) heats the crucible beneath a 15-inch funnel (paraffine-coated), through which a stream of carbon dioxide flows. The crucible is supported in a hole in a square of asbestos board, on which the inverted funnel rests. This is a simple, and should be an effective, arrangement.

If an appreciable amount of sulphur as sulphides exists in the rock, regard must be had to the iron in combination with it. If pyrrhotite is the only sulphide present, this will be decomposed by the mixture of acids in the determination of ferrous oxide, and the iron will appear as FeO. The sulphur may be either stated as S in the analysis, or the amount of iron necessary, for the molecule Fe_7S_8 of pyrrhotite calculated and deducted from the amount of FeO, and the percentage of pyrrhotite given. The former procedure is rather the better. If the only sulphide is pyrite, this will not be attacked in the determination of FeO, but the iron in this mineral will appear as Fe_2O_3. This may be accorded treatment similar to the iron in pyrrhotite. If both sulphides are

[1] J. H. Pratt, Am. Jour. Sci. (3) **48**, p. 149, 1894.

[2] Hillebrand, p. 167.

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present, it will be impossible to estimate the real correction unless the relative amounts of the two minerals are known. Fortunately this is seldom needed, and in general the amount of sulphur is so small that corrections for it are not often necessary.

13. Potash and Soda [1]

Two prominent methods are available for the determination of the soda and potash. They differ in the means employed for the decomposition of the rock and for the elimination of all the other constituents, the object of both being to obtain the alkali metals alone in solution as chlorides, and the final separation of these.

In the older method the rock powder is decomposed by a mixture of sulphuric and hydrofluoric acids, or by fusion with bismuth, lead, or boric oxides, digestion with the acid mixture being that most used. The solution obtained from this is treated successively with ammonia and with ammonium oxalate to remove silica, alumina, iron, titanium, phosphorus and lime. The magnesia is separated by one of several reagents (most often by the use of HgO), the sulphuric acid is removed by lead acetate or barium chloride, and the alkalies are determined in the filtrate as in the method described below. Or barium hydrate may be used to separate the other constituents from the alkalies (Classen). It is clear that any of these processes is long and complex, and that, not only do they suffer from the length of time needed, but that there is danger of loss of alkalies during the blasting necessary with some of the fluxes. Still more, the final solution is liable to be contaminated by alkalies derived from the many reagents used and taken up from the glass vessels. This method should never be used; in the United States it has been completely superseded by the Smith method.

The second method is that of J. Lawrence Smith.[2] It consists in decomposing the rock by heating with calcium carbonate and ammonium chloride, leaching with water from the insoluble silicate and aluminate of calcium, and carbonates of iron, cal-

[1] For the Smith method see: J. L. Smith, Am. Jour Sci., **1**, p. 269, 1871; Classen, **2**, pp. 613–615; Fresenius, **1**, pp. 519–520; Hillebrand, pp. 171–174; Mellor, pp. 222–226, 231–237; Treadwell, **2**, pp. 496–499.

[2] J. L. Smith, Am. Jour. Sci., **1**, p. 269, 1871.

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cium and magnesium, precipitation of the rest of the lime by ammonium carbonate, expulsion of ammonium salts by heating the evaporated filtrate, and final separation of the alkalies by chloroplatinic acid.

The advantages of this method are: its convenience and expedition, the manipulations being few, and a day and a half or two days being ample for the complete determination; the separation of magnesia at the start, which is a troublesome constituent to separate from the alkalies by the other methods; the small danger of introduction of alkalies from reagents or glass vessels, and, finally, its great accuracy, which is fully equal, if not superior, to that of the older methods.[1] The only real objection which can be urged against this method, as compared with the other, is the difficulty of obtaining a calcium carbonate entirely free from alkalies. The amount of these, however, is easily rendered extremely small by prolonged washing, and it is a constant error, the correction for which can be safely applied when once determined for the stock of calcium carbonate. Even if this is not done, however, it is certain that the errors involved will be less than those incident to the other methods if care be employed in the preparation of the calcium carbonate.

This method is practically the only one which has been used by the chemists of the U. S. Geological Survey, of the extreme accuracy and almost uniquely high character of whose analyses there can be no question. It is likewise the method which I have adopted exclusively, and which is almost universally employed in this country. In Europe, on the other hand, it seems to be less well known, or at least little used, and its undoubted merit and superiority over the other are not so generally recognized. Only the J. Lawrence Smith method will be described here.

Errors.—An inherent error is that the calcium carbonate used is seldom to be obtained entirely free from alkalies, very small amounts of sodium, and much less potassium carbonate being present. These can be reduced to negligible amount by thorough washing of the properly precipitated carbonate with hot water, but even if they are present they are of slight importance, as their amount can be determined once for all in the stock of

[1] Cf. J. L. Smith, loc. cit.; Hillebrand, Bull. 422, p. 171; M. Dittrich, Neues Jahrbuch, **2**, p. 81, 1903.

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calcium carbonate and an appropriate correction is easily and safely applied. If the calcium carbonate is properly prepared and well washed, the error involved by neglect to apply this correction will seldom be serious.

Another source of error is the retention of alkalies in the fused cake. This has been investigated by Hunter [1] and Connor.[2] Their results show that there is apt to be such a loss, as was already pointed out by Smith. As their results differ in magnitude, they indicate that the loss is dependent on the manipulation. If the process is properly carried out the loss should be small, but in highly accurate work the washed cake should be again treated with some ammonium chloride and a little additional calcium carbonate.

Overheating of the crucible during the sintering with calcium carbonate, overheating or too rapid heating of the basin during the driving off of the ammonium chloride, or of the crucible in drying the mixed chlorides, are all liable to lead to vaporization of the sodium and potassium chlorides. This can be entirely prevented by careful attention to the conditions of heating as described on later pages. Loss by decrepitation of the chlorides is to be guarded against.

The weight of the carbon sometimes found in the final mixed chlorides is so small as to be negligible, as shown by Smith and confirmed by my own experience.

Smith Method.—For the determination of the alkalies a specially ground portion of rock powder is to be used. Although Smith states that this is not absolutely necessary in all cases, yet it is certainly advisable, as complete decomposition can be secured at a lower temperature and with more certainty than if the powder be coarse.

A little more than 1 gram of the rock powder is ground down by hand in a small agate mortar, the grinding being continued until a small pinch causes no gritty feeling when rubbed on a tender part of the skin, such as the web connecting the thumb and the index finger or the inside of the wrist. It is then placed in a small special specimen tube, corked and numbered. No appreciable error due to partial oxidation of the FeO is to be feared

[1] See Mellor, p. 225.

[2] M. F. Connor, XII Cong. Geol. Int., C. R., p. 888, 1914.

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by this procedure, and it does not involve the great chance of loss of the fine powder incident to the method of first weighing out the coarse powder and subsequent grinding. About one-half of this powder will serve for the ferrous oxide determination, if such specially ground powder is to be used for this. About ½ gram is used for the alkali determination.

As the rock powder has to be more than ordinarily well mixed with the flux, the preparation of the portion used demands a procedure different from that used for the portions for other constituents.

If the analyst has had some experience, the portion may be weighed out by the method by subtraction described on p. 130. Special care must be taken to prevent loss of any of the fine powder.

The small tube containing the specially ground powder is wiped perfectly dry, uncorked, placed on the pan on the small frame intended for this purpose and weighed.

After weighing, and noting the weight as Tube+Subst., a half-gram weight is removed from the right-hand pan, and about half a gram of powder is carefully poured out into the platinum basin. This must be done with care to avoid any loss of powder, and when a sufficient quantity has been poured out, the tube is to be gently tilted up and lightly tapped to bring the powder down toward the bottom, the mouth being held over the basin. Not more than 0.6 gram need be taken, but not less than 0.45 gram. Half a gram is quite sufficient to yield results fully as accurate as 1 gram, and the consequent saving of platinum as well as shortening of the time needed for the determination are rather important considerations. The tube (still uncorked) is then weighed again, and the difference between this weight, recorded as Tube−Subst., and the former gives the weight of powder taken.

Just as in the weighing out of the powder for the alkali carbonate fusion, it may be necessary to shake out and weigh additional small portions several times. The endeavor should be made to get the final weight only slightly above, and as near to 0.5 gram as possible without undue loss of time. A little practice enables one to do this very quickly.

Under no circumstances is any powder to be taken up with the spatula and replaced in the tube, so as to bring the weight down

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to nearly ½ gram in case too much has been poured out. If this last has been done, either the determination is to be made on the somewhat large amount, which will be not at all objectionable, or the powder is poured back into the tube, the basin wiped out carefully, and the weighing done again, more care being taken this time in pouring out the powder.

One must be especially careful to avoid any loss by wafting away of the fine powder. The breath should not be directed toward the basin while the powder is being poured out, and the basin is to be covered with a watch-glass immediately after.

The balance-pans are then cleared of frame and weights, the pair of balanced watch-glasses are substituted, and an amount of dry ammonium chloride equal to that of the rock powder taken is weighed out. It is not necessary that this weight be exact, and it may be a decigram or some more, but should not be less. This is poured into the basin, above the heap of rock powder, but very slowly so as not to disturb and lose any of this.

The beginner would best use the other method and weigh out about ½ gram into the 30-cc. platinum crucible that is later to be used for the fusion. This weighing is by the method by addition, described on p. 129. About ½ gram of ammonium chloride is then roughly weighed out into the crucible above the rock powder, with precautions to avoid loss of the latter. If too much of the chloride is poured in, the excess should not be removed, for fear that some of the rock powder might be taken out at the same time. A small excess of the chloride does no harm.

The rock powder and the ammonium chloride are well mixed in the crucible with the small end of the platinum spatula, the slight dampness of the ammonium salt serving to prevent loss of the rock powder. The end of the spatula is cleaned off on a little ammonium chloride (in the watch-glass) which is added to that in the crucible. The platinum basin is inverted over the crucible and the whole turned over, so that the powder falls into the basin without loss. The basin is covered and the rest of the procedure is the same whatever method of weighing has been used.

The use of the platinum basin is preferred as a mixing-vessel to that of a large agate mortar, as recommended by Hillebrand, because, while the mixture may be made just as thorough, there is less liability to loss owing to the high sides of the basin, and

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because the mixed powders are transferred far more easily and safely to the crucible from the basin than from the mortar. I also prefer to have the powder ground specially fine before weighing, instead of after, as recommended by Hillebrand, as the latter is almost certain to lead to loss.

Whichever be the method of weighing used, the rock powder and the ammonium chloride are thoroughly mixed, by rubbing with the small agate pestle. This mixing must be very thorough and must be effected without any loss of powder. Attention should be paid to the powder at the sides, and an epicycloidal motion is effective.

An amount of calcium carbonate equal to eight times the weight of rock powder (about 4 grams) is then weighed on one of the pair of watch-glasses. If a correction for the small amount of alkalies present is to be made this weighing should be carried out to centigrams, but if not, the weighing need be only approximate, but should be more, rather than less than the required amount. With basic rocks 5 grams should be used, to prevent too great fluidity during the fusion. A small amount of calcium carbonate is transferred by the platinum spatula to an unweighed 30-c.c. platinum crucible, just sufficient to cover the bottom, and pressed lightly down with the small agate pestle. This prevents any adhesion of the fused cake to the bottom of the crucible.

After the rock powder has been mixed with the ammonium chloride, the mixture is mixed with the greater part of the calcium carbonate, also in the platinum basin. It is best to add the carbonate in two or three portions, and the rubbing with the pestle must be carefully but thoroughly done. The object is to have, so far as possible, some ammonium chloride and calcium carbonate in contact with each particle of rock.

When the mixing is considered complete, it is well to continue it for a few minutes longer. The pestle is laid down with its lower end in the watch-glass, and the mixture is poured cautiously through the lip of the basin into the crucible.[1] This transfer is aided by the platinum spatula in brushing down small lumps, and by final gentle tapping of the spatula on the inside of the basin, so as to cause the whole to pass through the lip without

[1] It is best to place the crucible on a 6-inch square of clean paper, so that any powder falling outside it may be recovered.

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loss outside the crucible. The contents of the crucible are then smoothed down with the spatula, the remaining calcium carbonate is poured into the basin and the latter rinsed with it by means of the pestle, which is also cleaned at the same time. The spatula is cleaned by rubbing against the carbonate in the basin, and the final portion of this is transferred as before into the crucible.

If the rock is specially ground as fine as has been described, the decomposition will be complete at a temperature not high enough to vaporize the alkali chlorides. An ordinary crucible may, therefore, be employed, with a well-fitting cover, instead of the capped conical one recommended by Smith and by Hillebrand, which permits a higher temperature for the sintering. The latter is, of course, to be preferred, but it is a somewhat expensive, and otherwise unnecessary, piece of platinum, so that it is as well to know that perfectly satisfactory results may be obtained without its use.

The crucible is covered and heated over a low flame for ten minutes or so, until no more vapors of ammonia or ammonium chloride are given off. The heating is then continued over the one-third full flame of a Bunsen burner, only the lower third of the crucible being heated to a not very bright red, and the crucible being kept well covered. This is continued for three-quarters of an hour, when the crucible is allowed to cool.

When cold, the mass is soaked in the crucible with just enough water to cover it, and the quicklime that has been formed is allowed to slake, by which the disintegration is rendered almost complete.[1] By the aid of the platinum spatula and a little water from the wash-bottle the contents of the crucible are easily transferred to the platinum basin, any adhering portions being removed by the spatula. A little water is allowed to remain in the crucible to soak it out. The spatula is rinsed off into the basin, which should contain not more than about 50 c.c. of water.

The partially disintegrated mass is well rubbed up with the agate pestle, the pestle rinsed off with a little water, the water in the crucible added, and the contents of the basin are brought to a boil, which should be continued gently for a few minutes. The liquid is then decanted through a 9-cm. filter into a 600-c.c.

[1] If the rock contains much iron the cake will have been more or less fused, and so the disintegration will not be as complete as it is with most rocks.

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beaker.[1] The stirring-rod is rinsed off into the basin, and the mass once more rubbed up with the pestle till there are no more lumps, the pestle is finally rinsed and the basin again heated. The liquid is decanted through the filter, the powder once more heated to boiling with a little water, and finally the contents of the basin are brought on the filter. The basin is rinsed, and the contents of the filter are washed with hot water, in small portions at a time, the powder being well stirred up by the first additions of water from the wash-bottle.

It is impossible to ascertain when the washing is complete by acidifying drops of the filtrate with nitric acid and testing with silver nitrate, as an oxychloride of calcium is formed which dissolves slowly in water, and will thus give a reaction for chlorine long after all alkalies are washed out. Smith states that complete washing is effected with 200 c.c. of water, but it is as well to be on the safe side and to use 250 to 300 c.c., which will make complete washing certain. This volume may be conveniently marked on the 600-c.c. beaker used for this operation by a thin line of paint.

It will be well for the beginner to test the thoroughness of the decomposition by dissolving a portion of the moist mass on the filter in hydrochloric acid. Solution will be complete if the fusion has been properly effected.

To the filtrate a little ammonia water is added and the liquid brought to a boil.[2] About 1.5 to 2 grams of ammonium carbonate previously dissolved in 25 c.c. of water[3] are then added, and the boiling is continued for a minute or so. The lime is thus completely precipitated, with the exception of a trace which is separated later, and the alkalies are left in solution as chlorides, along with ammonia chloride.

The bulky precipitate of calcium carbonate is allowed to settle

[1] One may advantageously use a 400-c.c. beaker of fused silica, so as to avoid contamination by glass.

[2] Addition of ammonia is necessary to prevent the formation of soluble calcium bicarbonate. The iridescent scum on the surface of the liquid is, of course, due to the action of atmospheric CO_2 on the calcium hydroxide and chloride.

[3] The solution of this should be begun when the crucible is put over the flame, so as to have it complete in time. It cannot be hastened by heating, as this decomposes the ammonium carbonate.

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a little, and is then filtered through a 9-cm. filter into a capacious basin (500 c.c.). This is preferably of platinum, but as such a large one would be very expensive, a fused silica basin can be used with equal accuracy. In default of this a glazed porcelain basin will answer, with but slight danger of contamination by alkalies taken up from the glaze. A glass basin must not be used on any account, as the liquid will be seriously contaminated with alkalies derived from it.

The precipitate is all brought on the filter, the beaker rinsed and the contents of the filter are washed with hot water in small portions at a time, till there is no chlorine reaction. The volume of liquid in the basin should be from 300 to 400 c.c. The basin is placed on the water-bath. It is best to leave it covered with a large watch-glass for ten minutes, as the excess of ammonium carbonate is decomposed by the heat and the liquid effervesces. When this is finished, the cover is rinsed into the basin, and the liquid is evaporated down to dryness, which should be complete, as indicated by the white color of the salts. This may be done conveniently by leaving on the water-bath over night.

The drying may be hastened materially by adding about 10 c.c. of alcohol when the contents of the basin are almost dry, and heating to dryness on the water-bath. There is thus also less liability to decrepitation.

If desired the contents of the large basin after evaporation down to about 50 c.c. may be transferred to the platinum basin used for the mixing of the powder and flux, and the evaporation to dryness carried out in this.

The basin, covered with a dry watch-glass, is then placed on a square of gauze over a low flame and heated gently. This heating must be cautious, and if there is any decrepitation, due to incomplete drying, it should be interrupted frequently till the decrepitation subsides, or otherwise particles of the salts may be thrown up and stick to the cover-glass. If the cover is slightly dewed with moisture at first, it is well to remove it frequently and wipe the moisture off quickly, so as to avoid such a mishap. When decrepitation has wholly ceased and white vapors of ammonium chloride begin to rise, the cover is taken off, the wire gauze removed, the basin being left on the ring of the retort stand. The upper sides are gently warmed by a half-full flame of the Bunsen burner, which

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is waved over the surface until the sides are free from ammonium chloride.

The salts at the bottom are next subjected to the same operation till no more white vapors are given off. Great care must be taken that the bottom of the basin is not overheated so that the salts melt and lead to the possible vaporization of alkali chlorides. During this process the clear white mass becomes dark and dirty-looking, from carbonization of the traces of organic matter which even very pure ammonium carbonate usually contains. Prolonged gentle heating will cause this to disappear to a large extent, but as the carbon is removed by filtration its disappearance at this stage is not necessary.

After cooling, a little water is added, just enough to dissolve the chlorides. If the rock contains sulphides, and especially if haüyne or noselite are present, a drop of barium-chloride solution is added to precipitate the sulphuric acid, which would otherwise appear later as sodium sulphate and lead to slight error. A few drops of the solution of ammonium carbonate are then added to precipitate the excess of barium and small amount of lime which is always present in traces at this stage; or, if no sulphates are present, a drop of ammonium oxalate solution is also added, as this precipitates calcium more completely than the carbonate. After rinsing the interior, as high as the salts extend, by gentle rocking and tipping of the small bulk of liquid, so as to ensure their complete solution, the basin is placed on the water-bath and evaporated again almost to dryness.

Two or 3 c.c. of water are then poured in to dissolve the salts, and the small amount of liquid is filtered through a $5\frac{1}{2}$-cm. filter placed in a $3\frac{1}{2}$-cm. funnel, without suction-tube, into a previously ignited and weighed 35-c.c. crucible. The greatest care must be taken in pouring out the first portion of liquid, as drops are apt to fly out of the filter if they fall from a height. The loss of a single one at this stage would cause so relatively large a loss of the small bulk of concentrated solution as to necessitate beginning the determination over again from the start. This may be prevented by using a small stirring-rod, with which a path of liquid is streaked to the lip, having the rod wet and its end touching the filter paper. The basin and filter are washed at least half a dozen times, preferably with warm water, and using only as little as

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possible, not over 3 or 4 c.c. at a time. When the washing is complete, as shown by a test for chlorine on a single drop toward the last, the crucible should not be more than three-quarters full.

A drop of dilute HCl may be added to the crucible, to decompose any alkali carbonates possibly present, it is placed on the water-bath, and the liquid is evaporated to complete dryness. Care must be taken to ensure this, as small amounts of water caught under the crust resist evaporation for a considerable length of time. It is not advisable, either here or in the evaporation in the basin, to use a platinum spatula or wire to break up the crust and hasten the operation, on account of the danger of loss of substance. The contents of the crucible can usually be rendered dry in three hours or so, if the water be kept at a brisk boil, or may be left over night.

When dry, the crucible is placed on a platinum triangle, covered, and very gently heated with a small flame, held in the hand and moved about at some distance beneath. When the slight decrepitation ceases and vapors of ammonium chloride rise, the flame is gradually raised (but not as far as the crucible bottom), till no more vapors are given off, as may be ascertained by lifting the cover from time to time. The cover is then freed from ammonium chloride by heating over the flame, and the sides of the crucible are similarly treated. The salts at the bottom are then most cautiously heated with the small flame till no more vapors are given off and the salts *just* begin to melt in places. When this happens the flame is to be removed instantly. The bottom of the crucible should not be heated above a very faint red, scarcely visible in daylight.

It is to be remembered that one has, on the one hand, to ensure the dryness of the salts and the complete expulsion of ammonium chloride, which would later be precipitated with the potassium platinichloride; and on the other, to avoid any vaporization of sodium or potassium chlorides, which, however, need not be feared if the chlorides are not heated above their melting-points.

If more than a few drops of ammonium carbonate or oxalate has been used to precipitate the traces of lime, the salts may be darkened by deposited carbon. This will usually be burnt off entirely, or nearly so, in the process of driving off the ammonium chloride and the incipient fusion of the alkali chlorides. The

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slight amount of it usually remaining is practically unweighable, as my experience has shown, and it may therefore be neglected.

The platinum crucible containing the salts is cooled in the desiccator, weighed quickly, and the weight recorded as Cruc. +NaCl+KCl. Five or 10 c.c. of water are poured in to dissolve the salts, and if the previous operations have been properly conducted the solution will be clear, or at most only a few flakes of carbonaceous matter will be present, which may be neglected as explained above, unless the extreme of accuracy be required. If, however, there is an insoluble residue of calcium carbonate the contents of the crucible must be again filtered, without addition of ammonium carbonate or oxalate, through a small filter into another weighed crucible, the filter washed, again evaporated to dryness, and the operation repeated as before. The crucible and its now perfectly pure contents are weighed, and this weight and that of the new crucible substituted for the former ones. It will be found that the difference seldom amounts to more than a few tenths of a milligram.

Separation of Potash.—We have now to separate the potash and soda so as to determine each of them. For this there are two appropriate reagents.

The one that is by far the best and most used is chloroplatinic acid, which converts the alkali chlorides into platinichlorides.[1] Potassium platinichloride is practically insoluble in strong alcohol, in which the sodium salt dissolves readily. This reagent, however, suffers under the disadvantage of expensiveness.[2]

The other reagent is perchloric acid, potassium perchlorate

[1] The term " platinichloride " is used instead of the more common " chloroplatinate " because it is in analogy with the common names of other double salts of the same or similar type; such as the silicofluorides, titanofluorides, aurichlorides, platinocyanides, cobalticyanides, ferricyanides, ferrocyanides, and many others. As the acids of these are not oxy-acids, and do not contain an element that replaces oxygen (as in the thiocyanates), the termination -ate is not appropriate. " Chloroplatinate " and the names of similar salts of other such acids of the platinum group are anomalous, and would seem to have no excuse for being except custom and euphony. " Platinichloride " is the form used by the Chemical Society of London.

[2] Winter (Jour. Ind. Eng. Chem., 8, p. 87, 1916) calculated from the loss in unrecovered platinum and the cost of recovery after 670 determinations that the cost of each was $0.0194 (less than two cents), the price of platinum being reckoned at $1.80 per gram.

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being practically insoluble, and sodium perchlorate easily soluble, in strong alcohol containing a little perchloric acid.

The perchlorate method is said to be almost, if not quite, as accurate as the platinichloride method. But as I have used the latter exclusively it will here be described in detail, and the perchlorate method will be more briefly treated.[1]

Separation as Platinichloride.—The dried and weighed chlorides as obtained above (p. 202) are dissolved in the crucible with about 5 c.c. of water, and to this, the requisite amount of a solution of chloroplatinic acid is added.

While it is necessary to add more than enough of this reagent to change the entire amount of both sodium and potassium chlorides into platinichlorides, yet any large excess is to be avoided, on account of the high cost of chloroplatinic acid, if for no other reason. We therefore use a solution of chloroplatinic acid made up to contain 0.05 gram of platinum to the cubic centimeter, as described elsewhere (p. 50). As it will take 3.36 c.c. of this to react completely with 0.1 gram of NaCl to form Na_2PtCl_6, and only 2.62 to do the same with KCl to form K_2PtCl_6, and as nearly all rocks contain both alkalies, we are sure of an excess if we assume that the chlorides are wholly sodium chloride, and calculate the amount of chloroplatinic acid solution used on this basis. We, therefore, multiply the weight of the combined chlorides by 34, and the result will be the number of cubic centimeters of platinum solution which is to be added. If the rock is extremely rich in sodic minerals, as albite or nephelite, with little or no potash, it will be well to take a few drops more than this.[2]

The crucible is then placed on the water-bath and heated, the water being allowed only to simmer, or attain at most a very gentle boiling, to avoid any dehydration of the sodium platinichloride, although I have never observed this to happen, even with a fairly brisk boiling. If the precipitated potassium platinichloride does not wholly dissolve when the liquid has become

[1] For the determination of the potash alone by the cobaltic nitrite method the student may consult Hillebrand, Bull. 422, p. 177; and Mellor, p. 540. I have never tried the method and therefore can not recommend it. See p. 208.

[2] The calculation need be only approximate. Thus, if the chlorides weigh .1273 gram we say $.13 \times 34 = 4.42$ c.c., and use a trifle more than 5½ c.c. of the platinum solution.

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warm, a few cubic centimeters of water are to be added to effect its solution. This will seldom be necessary if the directions and strengths of solutions given above are followed, even with highly potassic, leucite rocks.

The contents of the crucible are evaporated, with occasional slight shaking, to break up the crust as it forms, till the liquid is syrupy and the mass solidifies on cooling. This will take place when the depth of the liquid is reduced to about 2 mm., but is naturally dependent on the amount of alkalies in the rock. The evaporation should never be carried to complete dryness on the water-bath, as partial dehydration of the sodium salt will occur, the anhydrous sodium platinichloride being soluble with some difficulty in alcohol, and thus possibly adding to the apparent amount of potassium.

When the evaporation is finished the crucible is removed, covered, and allowed to cool, so as to make sure that the liquid solidifies. It is then half filled with alcohol of 0.86 specific gravity,[1] contained in a small wash-bottle, and allowed to soak. During this the Gooch crucible is prepared with an asbestos felt, as already described (p. 99), ignited, cooled and weighed, and placed in position in the filtering flask.[2]

By this time the disintegration of the solid mass in the crucible should be complete. If not, it may be hastened by stirring and rubbing cautiously with the lower end of a 5-c.c. pipette, the lower aperture of which should be from 1 to 2 mm. wide. When solution is complete, except for the precipitated, golden-yellow crystals of potassium platinichloride,[3] the suction is started

[1] If a hydrometer is not at hand an alcohol of approximately this specific gravity may be made by mixing five volumes of ordinary 95 per cent alcohol with one volume of water. Morozewicz (Bull. Acad. Sci. Crac., p. 796, 1906), has shown that, when Na_2PtCl_6 is present, alcohol stronger than 80 per cent decomposes the sodium salt, precipitating sodium chloride. An alcohol of less strength than 75 per cent dissolves appreciable amounts of K_2PtCl_6 (cf. Mellor, p. 231).

[2] If this has been previously used for the determination of magnesia, it, as well as the carbon filter and rubber, must be thoroughly washed free from all traces of ammonia.

[3] If the fluid is not yellow, or if small white grains (of sodium chloride) are present among the yellow crystals of K_2PtCl_6, there has not been enough platinum solution added. About 1 c.c. and a little water are to be added and the liquid again evaporated nearly to dryness.

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beneath the Gooch crucible and the fluid is transferred to it by means of the pipette. The crucible with the liquid is held in the left hand close to the Gooch, a little liquid sucked up into the pipette and allowed to run down the sides of the filter, to avoid breaking the felt. When all the liquid has been thus decanted, a little more alcohol is poured on the precipitate in the crucible, and decanted as before into the Gooch when this is empty. After three or four decantations, by which time the soluble salts are nearly gone and the liquid is almost colorless, the sides of the Gooch crucible are carefully washed down with a stream of alcohol and the pipette is rinsed both inside and out into the Gooch, which is filled with alcohol to wash the rim. The bulk of the precipitate is then transferred to the filter, without the use of a rod, by a gentle stream from the alcohol wash-bottle, the depth of liquid being so great that the drops can fall in the center without danger of breaking the felt.

With a slender stirring-rod capped with a bit of fine rubber tubing the small quantity of adhering potassium platinichloride is loosened and is washed into the filter, the stirring-rod being also rinsed off. Owing to the bright color and the high specific gravity of the precipitate, it is easy to be sure of its complete transfer. When the Gooch is again empty it is well washed, at least half a dozen times, the sides being also washed down, inside and out. Enough alcohol may be added each time to half fill the crucible, but it must be allowed to empty before another addition. After washing for the last time, aspiration is continued for a few minutes to partially dry the felt.

The final drying is accomplished in an air-bath at a temperature of 130°, which is necessary to drive off all the water. The bottom cap of the Gooch crucible is placed in position, and the crucible is covered while in the air-bath with a 7-cm. filter-paper instead of the cover. This permits evaporation, and at the same time guards against particles falling in from the top of the air-bath. The drying will usually be complete in half an hour, but it is as well after heating for this time and having been weighed, to reheat for another fifteen minutes, or to constant weight. After cooling in the desiccator the Gooch crucible is weighed, and recorded as Gooch$+K_2PtCl_6$. The weight of the potassium

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platinichloride is multiplied by 0.1938[1] to arrive at the weight of K_2O, from which is to be subtracted the amount of K_2O present in 4 grams of the calcium carbonate used, if this has been determined.

The weight of K_2PtCl_6 is then multiplied by 0.307 to reduce it to KCl, and the weight thus obtained is deducted from that of the mixed chlorides. The weight of the NaCl thus obtained is multiplied by 0.5308 to reduce it to Na_2O, which is to be corrected for the amount of Na_2O present in the calcium carbonate.

If a Gooch crucible is not available the method suggested by Hillebrand may be adopted. This consists in filtering off the excess of chloroplatinic acid solution through a small filter (5½ cm.) and washing with alcohol, as little of the precipitate as possible being brought on the filter. When the precipitate has been washed free from all soluble matter that which is on the filter is washed into the weighed crucible by small amounts of hot water, the excess of liquid is evaporated to dryness on the water-bath, and the precipitate is finally dried as above at 130°. Hillebrand prefers the use of porcelain for the evaporation of the alcoholic platinum solution, but for most work this is hardly necessary.

It is seen that the amount of Na_2O is determined by difference. But, in view of the accuracy of the method, this is preferable to a direct determination in the filtrate. If it is desired to do this, the filtrate is to be freed from platinum by one of the methods recommended by Hillebrand,[2] and the sodium is determined as sulphate in the usual way, by evaporation with sulphuric acid.

There is scarcely ever enough lithium present in igneous rocks to warrant its quantitative estimation. It is generally present in spectroscopic traces, but, so far, there seems to be no theoretical necessity of establishing this fact in every rock analysis. If it is desired to do this, the filtrate from the potassium platinichloride is to be evaporated to dryness and tested with the spectroscope. If it be desired to estimate it quantitatively, Hillebrand's directions and his summary of Gooch's method are to be followed.[3]

[1] For a discussion of the proper factors see Mellor, pp. 233, 250.
[2] Hillebrand, p. 174.
[3] Ibid., p. 175.

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All the platinum residues, both the platinichloride in the Gooch crucible and the filtrates, should be preserved in a wide-mouth bottle. The platinum may be recovered from time to time by the usual methods.[1]

Separation as Perchlorate.—As I have not personally tested this method, which has recently come into prominence because of the high cost of platinum, I shall base the brief description on the authorities cited below.[2]

The alkalies are obtained in the form of mixed chlorides, free from ammonium chloride, by the Smith method described above, so that we start with these in the platinum crucible after weighing (p. 202).

The chlorides are dissolved in the crucible in 10 to 20 c.c. of water, and more than enough perchloric acid[3] solution added to combine with the chlorides. About 1 c.c. of 20 per cent, or 0.7 c.c. of 30 per cent acid for each 0.1 gram of mixed chlorides will suffice. The liquid is then evaporated in the crucible until fumes of perchloric acid appear. Ten c.c. of water and a little more perchloric acid are again added and the solution is evaporated until the white fumes are seen.[4] If white fumes do not appear a little more water and perchloric acid are to be added and the procedure is repeated. The crystals should be kept broken up, but not reduced to a fine powder, during the last evaporation.

After cooling, the mass is treated with about 20 c.c. of alcohol containing 0.2 per cent of perchloric acid, and filtered through a weighed Gooch crucible. The perchlorate crystals are washed two or three times by decantation, and three or four times on the filter, with the 0.2 per cent solution of perchloric acid in alcohol. It is then dried at 130° for one-half to one hour and weighed, as $KClO_4$. Multiplying this weight by the factor .3176 reduces it to K_2O, and by .5956 to KCl.

If the volume of washing liquid is kept small, as can easily be

[1] Classen, **2**, p. 262; Mellor, p. 240 .

[2] Mellor, p. 237; Treadwell, **2**, p. 50, Baxter and Kobayashi, Jour. Am. Chem. Soc., **39**, p. 249, 1917; Gooch and Blake, Am. Jour. Sci., **44**, p. 381, 1917. Other references will be found in these papers.

[3] The preparation of this is described on p. 52. Perchloric acid of 30 per cent has a specific gravity of 1.20, that of 20 per cent, 1.12.

[4] It would appear that for the amounts of alkalies found in rocks only one evaporation will usually be sufficient, but it is safer to evaporate twice.

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done, " the solubility of the precipitated perchlorate is insignificant for practical purposes."

Alcoholic solutions of perchloric acid are liable to explode on evaporation, especially over a free flame. They should, therefore, be allowed to evaporate spontaneously.

Determination of Potash Alone.—In technical work the determination of potash in silicates without regard to the soda, is sometimes called for. In this case ½ gram of the rock powder is decomposed by a mixture of dilute (1 : 1) sulphuric and hydrofluoric acids, and the hydrofluoric acid is driven off by several evaporations. The potash may then be separated by the sodium cobaltinitrite method,[1] and determined either as platinichloride or as perchlorate.

A much more rapid method, and one giving very accurate results, is that suggested by Hicks and Bailey,[2] and now used in the U. S. Geological Survey laboratory for the determination of potash in glauconite and such materials. I have had experience with it, with satisfactory results.

After decomposition with sulphuric and hydrofluoric acids, the dried residue is dissolved in dilute hydrochloric acid. After filtering, this solution is evaporated to dryness with the addition of a slight excess of chloroplatinic acid. The residue is washed on a small paper filter with alcohol containing 2 per cent of concentrated hydrochloric acid until free from excess of chloroplatinic acid and platinichlorides. The potassium platinichloride is washed through the filter with hot water, the platinichloride reduced to metallic platinum by magnesium, and the platinum is weighed. Multiplication of the weight of platinum by 0.4826 gives the weight of K_2O. For details the original paper may be consulted.

14. Hygroscopic Water[3]

By this term is meant the moisture which is adsorbed by the rock powder from the atmosphere, or which may come from that enclosed in microscopic cavities, and a part of the more loosely combined water of crystallization of some zeolites and other

[1] Cf. Hillebrand, Bull. 422, p. 177; Mellor, p. 540.

[2] Hicks and Bailey, in U. S. Geol. Surv., Bull. 660–B, p. 53, 1917.

[3] Fresenius, **1**, p. 74; Hillebrand, pp. 69–70; Mellor, pp. 155–157.

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hydrous minerals may also be included under this head. It is all, or nearly all, expelled from the rock at temperatures of about 110°, though Day and Allen [1] conclude from their study of feldspar powders that some of it is not expelled below 600° to 800°. The amount of hygroscopic water in fresh rocks is usually very small, and Day and Allen [1] note that the quantities of adsorbed water determined by them "are of the same order of magnitude as those usually obtained for the water content in feldspar analyses." Notwithstanding this, it is always well to determine hygroscopic water separately from combined water. The reasons for this have been fully discussed by Hillebrand [2] and need not be gone into here.

The influence of the fineness of the powder on the adsorption of moisture from the atmosphere, and the consequent advisability of analyzing air-dry material, have already been mentioned (pp. 66, 72).

About 1 gram of the rock powder is weighed out into a previously ignited and cooled platinum crucible of 30 or 40 c.c. capacity and this is heated in an air-bath at a temperature a little above that of boiling water. The exact temperature is of no great importance, as long as it is slightly above 100°. In the U. S. Geological Survey laboratory a toluene bath is used, giving a temperature of 105° (Hillebrand), while my practice is to use an ordinary copper air-bath, with single walls, and the flame so regulated as to maintain the temperature constantly at 110°, which is readily accomplished. The crucible is covered during the heating with a 7-cm. filter-paper, the platinum cover being removed. It will usually be found that half an hour's heating, and often less, will be sufficient to arrive at a constant weight. After heating, the crucible is allowed to cool in a desiccator and is weighed, heated again for a quarter of an hour, and if the weight is constant, the loss in weight, divided by the weight of rock powder taken, gives the percentage of hygroscopic water, which may be conveniently tabulated as H_2O-.

The portion used for this determination may be used for that of any other constituent, except alkalies and ferrous oxide. Indeed,

[1] Day and Allen, Isomorphism of the Felsdpars. Carnegie Publication No. 31, p. 57, 1905.

[2] Hillebrand, pp. 57–70.

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it is often a saving of time if this be done. Determinations that suggest themselves are those for the main sodium carbonate fusion, for manganese, and for baryta and zirconia.

15. Combined Water[1]

Under this head is included all the water in a rock which is chemically combined in mineral molecules, either as water of crystallization (as in analcite) or as hydroxyl (as in muscovite or biotite).

Few constituents of rocks have had the amount of time, thought, labor, and ingenuity in devising apparatus, expended on them that have been devoted to the accurate determination of combined water; and, in all the text-books, an amount of space and attention are devoted to it that is quite disproportionate with its importance in rock analysis.

In the analysis of minerals, in many of which the water or hydroxyl may play a very important part in the constitution of the molecule, the accurate determination of water may be (and often is) of very great importance for the correct interpretation of the composition and molecular constitution of the mineral. In fresh rocks, on the other hand, water is usually a constituent of very subsidiary and minor importance; so that the use of any of the very complicated forms of apparatus that have been devised is quite uncalled for, unless there is some special reason for going to all the trouble that they involve. Even with such rocks, the simple Penfield method, which is capable of great accuracy, will usually be found to be entirely adequate to the purpose.

Errors.—Because of its usually minor importance in the analysis of rocks, the errors involved in the determination of water will seldom be serious.

If the water is determined by loss on ignition, a plus error will be introduced by the expulsion of other volatilizable substances such as carbon dioxide, sulphur, or chlorine. Only that of the carbon dioxide is likely to be of serious consequence. The " hygroscopic " water will, of course, also be expelled, and should be

[1] Classen, **2**, pp. 626–634; Fresenius, **1**, pp. 72–78; Gooch, pp. 34–38; Hillebrand, Bull. 422, pp. 57–83; Mellor, pp. 157–159; 570–575; Treadwell, **2**, p. 512; S. L. Penfield, Am. Jour. Sci., **48**, pp. 30–37, 1894.

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allowed for. A minus error is introduced by oxidation of any ferrous oxide present; this may be so great that, if the rock contains much ferrous oxide and but little water (as may happen with basalts, for instance), there will be an actual gain, instead of loss, in weight on ignition.

If the water is determined by an absorption method, presence of moisture in the air used to pass through the apparatus will add to, and failure to expel or absorb all of the water will lessen, its apparent amount.

In the Penfield method the only notable source of error in general is that due to the presence of carbon dioxide in the substance. Unless this is allowed to escape from the tube that contains the water, its higher specific gravity as compared with that of air will diminish the apparent weight of water. A correction may be made for it, and Penfield's paper should be consulted on this point. For fresh rocks the error will be of no consequence.

In all water determinations in rocks or minerals, regard must be had for the very high temperature at which the hydroxyl is completely driven off (in the form of water) from some minerals, as with talc, topaz, chondrodite, or staurolite. For very exact determinations this point must be looked into, so that, if necessary, a sufficiently high temperature is used for complete expulsion.

Loss on Ignition.—The early method, and one very frequently used, even at the present day, for the determination of this combined water, is that of simple ignition in a platinum crucible, the assumption being that this "loss on ignition" represents only the total water in the rock. A little consideration shows that the results under these circumstances will only be accurate when the rock contains neither substances which are easily volatilizable at the temperature of ignition (as carbon dioxide, carbon and organic matter, sulphur, chlorine, or fluorine) nor oxidizable constituents (as ferrous oxide). In the former case the apparent amount of water will be too great, owing to the partial or entire loss of the volatilizable ingredients, and in the latter it will be too small, on account of the gain in weight through the oxidation of ferrous oxide to ferric.

It is held by some that the error due to the latter cause may be corrected by calculation of the gain in weight which the ferrous oxide that is present in the rock, and which is separately deter-

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mined, would undergo if completely oxidized to ferric oxide. This assumption, however, is by no means valid under the circumstances obtaining in the process of ignition,[1] as is shown, for example, by the difficulty of completely oxidizing magnetite by ordinary ignition, even after roasting with nitric acid.

In the case of volatilizable constituents, also, there can scarcely ever be a certainty that their loss in this way will be complete, so that appropriate corrections may be made with safety after their separate determination. This would be true only of carbon dioxide when derived from calcite, magnesite, or dolomite, and then only after prolonged blasting.

This being so, and it being also a fact that there are few rocks which contain no such disturbing constituents (especially FeO), it follows that with the great majority the combined water should not be determined by loss on ignition.

As, however, the determination of combined water is not always of great importance for the chemical study of rocks, it happens that this simple method may be used in certain cases. These would include very fresh igneous rocks, that contain but a small amount of water, no other volatilizable ingredients, and only a small amount of ferromagnesian minerals, say up to 5 per cent, and consequently only 1 or 2 per cent of ferrous oxide. Many granites, porphyries, syenites, trachytes, rhyolites, andesites, and anorthosites fall under this description. For such rocks the minute error due to the very small amount of ferrous oxide present (amounting at most to one-ninth of its weight) may be deemed to be negligible, and the results of such a determination may be regarded as acceptable.

If the method of "loss on ignition" is to be employed, the weighed crucible and its contents, which have previously been used for the determination of hygroscopic water,[2] are ignited (covered) at a bright-red heat for about half an hour, or to constant weight, cooled in the desiccator and weighed. The loss in weight represents the amount of combined water. The fact must,

[1] Cf. Sosman and Hostetter, Jour. Am. Chem. Soc., **38**, p. 820, 1916; Trans. Am. Inst. Min. Eng., p. 907, 1917.

[2] It is not advisable to use a portion in which any other than hygroscopic water is determined, as the rock powder is apt to sinter through the great heat and be attacked with difficulty by fluxes. A separate portion may be used.

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however, be recognized that this method of procedure is not strictly accurate, and that for all high-class work, and in all rocks where the amount of ferrous oxide is at all considerable, or, if volatilizable substances are present, the combined water should be determined directly.

Penfield's Method.—The general inadvisability of employing any of the more complex methods spoken of above, and some of which are described in the authors cited, has already been mentioned. Fortunately, a very simple and accurate method has been devised by Penfield,[1] which meets all the requirements with the great majority of rocks, needs no elaborate apparatus, and takes but about half an hour for its execution. It would seem to be little known,[2] much less than it deserves to be.

This consists in igniting the rock powder in a tube of hard glass, closed at one end and with or without enlargements in the middle, pulling off the heated end containing the powder, weighing the portion of the tube which contains the expelled water, and finally weighing this portion of the tube after thorough drying. This gives the total amount of water, hygroscopic and combined, from which the amount of the former, as previously obtained, is to be deducted to obtain the latter. For illustrations of the apparatus used the reader is referred to the paper cited above.

With most fresh igneous rocks a simple tube of rather hard glass is used, closed at one end, and without any enlargement. The dimensions recommended by Penfield are 20 to 25 cm. long[3] and with an internal diameter of about 6 mm. If the rock contains more than a fraction of a per cent of water it is better to have a bulb or enlargement blown about midway in the tube. Indeed, this is always advisable, to guard against drops of water rolling back on the heated portion. A single bulb is sufficient for nearly all rocks, and the more complicated forms illustrated by Penfield will seldom be found necessary in rock analysis, unless the rock is not fresh.

[1] S. L. Penfield, Am. Jour. Sci., **48**, p. 30, 1894.

[2] Neither Classen, Fresenius, Gooch, Mellor nor Morse, mention it; while Hillebrand and Treadwell give but very brief descriptions.

[3] The tube must not be too long to go in the balance-case, and so interfere with weighing, nor too short, so as to give rise to the danger of loss of water through lack of sufficient cooling surface and heating of the cooler portion.

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It is of importance to have the tube thoroughly dry, and this " is best accomplished by heating and aspirating a current of air through it (while hot) by means of a glass tube reaching to the bottom." This should always be done, even if the tube is apparently dry. After cooling, the tube is weighed, its weight including that of the brass tube-support which is used to support it on the balance-pan.

From ½ to 1 gram of the rock powder is then introduced, filling the tube about 2 cm. from the closed end. This must be done without soiling the upper portion of the tube, and is accomplished by means of a small thistle-tube, of diameter small enough to slip easily into the bulbed tube, and long enough to reach the end. Such a filling-tube can be readily made from a 5-c.c. pipette by cutting the bulb in two and reducing the length of the tube to 25 cm. The filling-tube, of course, must also be thoroughly dry.[1] After the powder is introduced the tube is weighed again, to obtain the weight of substance used, the manipulation being delicate and gentle to avoid any rolling of the powder toward the open end.

After a few gentle taps to form a free passage above the powder for the heated air, which might otherwise drive the powder toward the bulb and so necessitate refilling and reweighing, the tube is held in a clamp horizontally, or *very slightly* sloping toward the mouth. A narrow strip of filter-paper or cloth, moistened with cold water and kept moist and cool, is wrapped around the bulb and the farther end of the tube, so as to ensure condensation of the expelled water, care being taken that it is not so near the mouth as to allow any water dropped on it to enter the tube.

A gentle heat is then applied to the closed end, and is gradually increased to the full heat of the Bunsen burner. The blast may be used if minerals are known to be present which only give off their water with difficulty, but this will not be needed in most rocks. If the strip of cloth or filter-paper be kept moist, there is scarcely need for a screen of asbestos board, nor is it often necessary to partially close the tube with another short piece of tube drawn out to a capillary and connected by rubber tubing. If the heated end of the tube tends to sink, this should

[1] The thistle-tube can be easily cleaned " by drawing through it a bit of cotton attached to a wire," or, if the analyst be a smoker, a fresh-pipe-cleaner will answer admirably.

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be remedied by gently turning it around from time to time parallel to its axis, the clamp being adjusted so as to allow of this being done.

After the whole extent of the powder has been ignited and the water completely expelled, which will take at least a quarter of an hour, a short piece of narrow tubing is melted onto the closed tip, to serve as a handle. The flame is then lowered and the water is very gently and gradually driven into the bulb. This must be carried out with caution and patience to avoid cracking the tube. When the water has been driven into the bulb and to a safe distance, the portion of the tube immediately in front of the powder is heated to softness all around, and the end containing the powder drawn off and the other part sealed without allowing the flame to enter. The tip of a Meker burner flame serves well for this.

The remaining portion of the tube containing the water is allowed to cool in the clamp in a horizontal position, is wiped clean and dry on the outside and weighed. It is well to test the water with blue and red litmus-paper after weighing. It is then placed again in the clamp and gently heated, the moist air and steam being sucked out by means of a small tube extending to the bottom and connected with a suction-pump. After thorough drying in this way it is allowed to cool and is again weighed.

The loss in weight is the amount of total water, which is reduced to percentage figures by division by the amount of substance taken; the percentage of hygroscopic water already determined is then subtracted.

In nearly all cases the simple method described above will be quite sufficient and will yield very accurate results. But when rocks, such as some metamorphic ones, contain minerals like talc, topaz, chondrodite, or staurolite, whose water is not completely driven off over the blast, it becomes necessary to use a more intense method of heating. For a description of this, reference may be made to Penfield's article.

If the rock contains constituents like SO_3, S, Cl or F in appreciable amount, which are volatile and which will add to the weight of the water driven off and condensed, it is necessary to use a retainer for these during the ignition. The best of these is lime, previously ignited and cooled.[1] A little of this is intro-

[1] Penfield and Howe (Am. Jour. Sci., **47**, p. 191, 1894) state that lead oxide which is often used, is wholly unsuitable.

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duced by means of the thistle-tube into the bulbed tube, after the rock powder has been weighed, and mixed " by means of a fine wire bent into a corkscrew coil at the end." A decigram or two will be ample for most rocks. In ordinary rock analysis the correction for CO_2, described by Penfield, will not be necessary.

16. Phosphorus Pentoxide[1]

As the amount of material is usually ample in rock analysis, it is best to determine phosphorus pentoxide in a separate portion of rock powder, although it can be determined m the solution used for the total iron oxides and titanium dioxide, as mentioned below.

Errors.—The chief errors to which the determination of phosphorus pentoxide is subject are caused by the somewhat uncertain compositions of the ammonium phosphomolybdate and ammonium magnesium phosphate precipitates, which vary according to the conditions that obtain during precipitation.

It is not necessary to go into the subject here, and the student will find details given by Mellor. The dependence of the composition of the magnesium precipitate on the conditions of precipitation has already been touched on (p. 180). It will suffice to say that the conditions laid down should be followed closely to obtain accurate results. Fortunately the amount of phosphorus in igneous rocks is generally small, so that errors in its determination are of subsidiary importance.

If considerable vanadium is present in the rock, a very rare occurrence, the percentage of V_2O_5 is to be subtracted from that of P_2O_5, as the vanadium is precipitated as vanadomolybdate along with the phosphomolybdate and weighed as magnesium vanadate,[2] with the magnesium phosphate if phosphorus is present in much greater quantity than the vanadium, as it invariably is in rocks.

Precipitation as Phosphomolybdate.—The phosphorus pentoxide is best separated from the other constituents present in the solution by the old and well-known method of precipitation as

[1] Classen, **2**, pp. 564–570; Fresenius, **1**, pp. 446–447; Gooch, pp. 81–82; Hillebrand, Bull. 422, pp. 144–146; Mellor, pp. 590–598; Treadwell, **2**, pp. 434–440.

[2] Cain and Hostetter, Tech. Pap. Bur. Stand., No. 8, 1912.

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phosphomolybdate. The conditions recommended for this vary considerably, but I have found that Woy's procedure is the most rapid and best.[1]

For the decomposition about 1 gram of rock powder is weighed out into a small platinum basin, or, if that is not available, into a capacious crucible. The rock powder is then mixed with 10 c.c. of water, taking the precautions to prevent loss of powder noted previously, and is stirred up with a small platinum spatula or platinum wire which is left in the basin for stirring. Ten c.c. of concentrated nitric acid are added, about 5 c.c. of hydrofluoric acid are next poured in, and the mixture is evaporated to dryness on the water-bath or over a low flame with occasional stirring. Evaporation with small quantities of nitric acid alone is repeated two or three times, to decompose the fluorides as completely as possible.

When completely dry after the last evaporation, the basin is heated till its contents become brown, and when cool the crust is moistened with 5 c.c. of a mixture of nitric acid diluted with twice its bulk of water, and gently boiled for a few minutes, to convert any meta- or pyro-phosphates, possibly produced by the heating, into orthophosphates. Solution will be complete, except for the silica and fluorides present. The liquid is now filtered through a 5½-cm. filter into a 150-c.c. beaker. The basin is to be rinsed out and the filter washed half a dozen times with the same warm dilute acid. The volume of the liquid should not be more than about 50 c.c.

About 25 c.c. of ammonium nitrate solution (containing 320 grams of ammonium nitrate to the liter) are added, and the liquid is heated until it is near boiling. A temperature of 60°–70° is appropriate. In the meantime 25 c.c.[2] of ammonium molybdate solution (p. 48) are heated to boiling, and poured in a thin stream down the stirring-rod into the hot liquid in the beaker, which is kept in constant rotation. Precipitation is immediate and complete.[3]

[1] Mellor, p. 595; Treadwell, 2, p. 436.

[2] If the rock contains more than 1 per cent of P_2O_5 50 c.c. must be used.

[3] The filtrate and washings from this precipitate should be kept (covered) for a few hours. If a yellow precipitate forms all the phosphorus has not been separated. The warmed filtrate must then be treated with more ammonium

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The liquid is then filtered through another 5½-cm. filter, the bright-yellow precipitate being disturbed as little as possible. The latter is washed with a mixture of weak solution of ammonium nitrate, nitric acid and ammonium molybdate solution in equal parts, till the addition of ammonia water in excess produces no permanent precipitate in a few drops of the filtrate in a watch-glass. About 50 c.c. of the washing mixture will usually be ample, and it should be prepared in a small beaker as needed.

The phosphorus is now all in the precipitate of ammonium phosphomolybdate, and the beaker containing the greater part of this is placed beneath the funnel, and the filter is then filled with ammonia water diluted with an equal amount of water. This dissolves the small portion of precipitate in the filter and part or the whole of that in the beaker, assisted by stirring. If solution is not complete some more ammonia must be added. The filter is then washed, half a dozen fillings with water being sufficient.[1]

If the fluid in the beaker is turbid, due to the formation of a white compound of phosphorus, as occasionally happens, this may be overcome by the addition of a small fragment of citric or tartaric acid. If this fails to remove the turbidity, the liquid is to be filtered through the same filter into another small beaker, the filter ignited in a small platinum crucible and fused with a pinch of sodium carbonate, the small cake dissolved in water, acidified with nitric acid, and the solution added to the rest (Hillebrand). This has never been necessary in my experience.

To the solution in the beaker, which may amount to 50–100 c.c., 10 c.c.[2] of "magnesia mixture" are added, best through the same filter, to remove any possible deposit in the "magnesia mixture." The beaker is allowed to stand for twelve hours; then the contents are filtered through a small filter and the precipitate collected on the latter, that adhering to the sides of the beaker being rubbed

molybdate and this precipitate filtered, washed, and treated like, and added to, the first.

[1] If it has been necessary to precipitate more phosphorus in the previous filtrate, the two solutions of phosphomolybdate are, of course, mixed and precipitated as above.

[2] If there is much phosphorus more magnesia mixture should be added. At least 1 c.c. of magnesia mixture is needed for each centigram of phosphorus pentoxide in the solution.

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off. The filter and precipitate of ammonium-magnesium phosphate are well washed with weak ammonia water.

The filter with its contents are then placed in a small weighed platinum crucible, and, after the filter has been carbonized, are ignited at a bright-red heat. When cool, the crucible and contents are weighed, and the weight of the $Mg_2P_2O_7$ is multiplied by 0.638 to reduce it to P_2O_5. The appropriate weight of P_2O_5 determined from this percentage is to be deducted from the weight of the precipitate by ammonia water (p. 59), to arrive at the correct weight of alumina.

The phosphorus may also be determined, more rapidly and about as accurately, as phosphomolybdic anhydride. For this procedure the yellow phosphomolybdate precipitate is collected in a weighed Gooch crucible and washed with a mixture of the ammonium nitrate solution and dilute nitric acid, about 50 c.c. being usually sufficient. The lower cap is then put on, and the crucible is gently heated until the contents are dry and no more vapors of ammonia or ammonium salts arise. The heat is then raised until the bottom is a dull red and this is continued until the yellow mass is entirely decomposed into the greenish-black anhydride, $24MoO_3.P_2O_5$. About ten minutes suffice for this. The weight of the anhydride multiplied by 0.0395, or by 0.04 for the usual small amounts, gives the weight of P_2O_5. According to my experience the method is rapid, accurate, and satisfactory.

If material is scanty and it is desired to determine phosphorus pentoxide in the solution used for total iron and for titanium dioxide, the following process will serve: The acid solution or an aliquot portion of it, after determination of titanium is precipitated with ammonia, the precipitate washed with hot water a few times, dissolved on the filter with dilute nitric acid and the filter washed; the filtrate and washings are evaporated to small bulk, and the phosphorus is precipitated in this by ammonium molybdate. The subsequent operations are as described above.

17. Manganous Oxide

Manganous oxide may be determined in the main portion used for silica, etc., if the basic acetate method has been used for its separation. This procedure will be described later (p. 223).

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For reasons already given, however, this method is to be avoided, and the manganous oxide is best determined in a separate portion by a colorimetric method, which is very accurate and serves admirably for the small amounts (less than 0.5 per cent) that are almost invariably found in igneous rocks. If the manganous oxide amounts to 2 per cent or more, as it may in some silicate minerals or in very exceptional rocks, it is best to separate it by the basic acetate method and determine it gravimetrically.

Errors.—There are no serious errors inherent in the colorimetric method, if the solution is properly and completely oxidized to permanganate, as can be readily accomplished if the directions given are followed.

The great liability to error involved in the basic acetate method has already been discussed in connection with alumina (p. 149). The error here, through weighing of alumina with the manganous oxide, may easily amount to many times the weight of the manganous oxide present. For this reason the high figures often reported for manganous oxide in rock analyses are regarded with more than suspicion.[1]

If manganous oxide is not separated and determined some of that present will be precipitated with and appear as alumina, probably because it is peroxidized. A smaller portion falls with the lime, and the rest—generally the largest portion—is precipitated with the magnesia.[2] As the amount of manganous oxide in igneous rocks is very small, seldom over 0.50 and usually under 0.20 per cent, this error will not be serious for the great majority of rocks (p. 14).

Colorimetric Method.[3]—This method, introduced by Walters, is based on the oxidation of manganous salts to permanganates by the action of ammonium persulphate in the presence of silver nitrate, which acts as a catalyzer, and the colorimetric comparison of the solution with a standard solution of permanganate.[4]

[1] Cf. H. S. Washington, Prof. Paper 99, pp. 17, 20, 21; Hillebrand *et al.*, Jour. Am. Chem. Soc., **28**, p. 233, 1906.

[2] Hillebrand, p. 114.

[3] H. E. Walters, Chem. News, **84**, p. 239, 1901; Classen, **1**, p. 487; Hillebrand, pp. 116–118; Mellor, pp. 382–384; Treadwell, **2**, p. 127.

[4] Lead peroxide, sodium bismuthate, or potassium periodate can be used as oxidizers, instead of ammonium persulphate. Lead peroxide needs no silver nitrate as a catalyzer, but the solution must be filtered.

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There are needed for this method a standard solution of manganous sulphate, containing 2 milligrams of MnO in 10 c.c., and a solution of silver nitrate, both of which have been described on pp. 51 and 54.

About 1 gram of the rock powder is weighed out into a capacious platinum crucible, or better, a small platinum basin, and 10 c.c. of sulphuric acid (1 : 1) and 5 c.c. of hydrofluoric acid are poured in. After thorough mixing with a small platinum spatula or wire, the mixture is heated gently until the powder is wholly decomposed, and then more strongly until white fumes of SO_3 are given off. After cooling, another 5 c.c. of dilute sulphuric acid are added and the heating repeated, this being done once or twice more to ensure the expulsion of the hydrofluoric acid. The last time it is best to heat almost to dryness. About 10 c.c. of nitric acid, which should be free from chlorine, and the same amount of water are added. The mixture is gently heated for ten minutes or so, to dissolve all manganese that may be present. The insoluble residue, chiefly calcium and possibly barium sulphates, is filtered off through a small filter and washed with small portions of hot water, the filtrate and washings being caught in a 150-c.c. beaker. They should not amount to more than about 50 c.c.

To the clear rock solution 10 c.c. of the silver nitrate solution are added for each milligram, or 0.10 per cent of manganese present in the rock. For very silicious rocks, as granites or rhyolites, 10 c.c. will be ample, but for most rocks 20 or 30 c.c. should be used. It is essential to have an excess of silver nitrate, and I, therefore, prefer a solution containing 3, rather than 2, grams to the liter. If there is a precipitate of silver chloride, as will happen if the rock contains sodalite or scapolite, the liquid is to be boiled and well stirred to coagulate the precipitate and filtered into another small beaker, the filter being washed twice with a little water.

Ten c.c. of dilute (1:1) sulphuric acid are poured in, about 2 grams of solid ammonium persulphate are added, and the beaker is gently heated over a low flame. The salt dissolves with a crackling noise, and as the liquid warms, the purple color of the permanganate appears, which gradually deepens until it attains a maximum. Soon after the color begins to appear, it is well to remove the beaker from the flame and place it in a basin con-

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taining some cool water until the color has reached its greatest depth.

With some rocks, or under certain conditions, the color of the liquid is a peculiar red, due possibly to the presence of manganic salts. If sufficient silver nitrate is present this will gradually change into the true purple of permanganate solutions. But to hasten matters, the solution may be decolorized by the cautious addition of a few drops of solution of sulphur dioxide, the addition of 5 or 10 c.c. of silver nitrate solution and another gram or so of persulphate. On heating, the proper color will now appear.

Sometimes, after the proper coloration has begun at the bottom, the rest of the liquid assumes a dirty brown color, due to the separation of manganese hydroxide. This may be caused by insufficient silver nitrate, but it is generally due to insufficiency of sulphuric acid. The liquid is cleared and decolorized by cautious addition of sulphur dioxide; 10 c.c. of dilute sulphuric acid and 5 c.c. of silver nitrate with about a gram of persulphate are added, and the solution brought to a boil. Sufficient sulphuric acid should always be added at the beginning to prevent this annoying discoloration, the rectification of which will add considerably to the volume of the liquid.

When the proper color has been obtained and the liquid has cooled to room temperature, the solution is poured into a 100-c.c. measuring-flask, with stopper, unless the rock contains much manganese, when a 200- or 250-c.c. flask is to be used. The solution will retain its full color unchanged for several days, the rapidity of the change being the less the stronger the solution, so that one should not dilute up to the mark until one is ready for the comparison, if a series of manganese determinations is to be carried out. The depth of color must, of course, be considerably lighter than that of the standard, so it is well not to dilute the test solution until the standard has been prepared.

In another 100-c.c. measuring-flask there are placed by means of a 10-c.c. pipette 10, 20, or 30 c.c. of the standard manganese solution, the amount depending on the depth of color of the test solution. The color of the standard, when oxidized to permanganate, must be considerably deeper than that of the test solution. Ten c.c. is usually enough. The required amount of silver nitrate solution, 20 c.c. for each 10 c.c. of manganese solution,

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10 c.c. of dilute sulphuric acid, and 2 grams of ammonium persulphate, are added. The solution is boiled and oxidized to the proper color exactly as with the test solution.

When cool the standard is diluted to the mark, thoroughly mixed, and poured into a burette. Ten c.c. are drawn off with a pipette into one of the rectangular glasses used in the titanium determination (p. 43). In the other glass is placed some or all of the test solution. The standard is now diluted with water from another burette until the color of the standard matches that of the test solution. The whole process is carried out exactly as was done with titanium. The calculation of the amount of manganese is exactly analogous to that of titanium, due regard being paid to the amount of standard manganese solution used.[1] If ammonium persulphate has been added prior to the precipitation of the main portion by ammonia, the weight of the manganese, calculated as Mn_3O_4 by multiplying the weight of MnO by 1.075, is to be subtracted from that of the ignited ammonia precipitate of alumina, etc.

Gravimetric Method.—If the basic acetate method has been used, and it is desired to determine manganese in the main portion, it may be done according to the following method described by Hillebrand[2] and used by him in cases where the colorimetric method is not applicable. For the reasons given on page 149 this gravimetric determination should not be used unless the analyst is forced to do so.

The combined filtrates from the precipitate of alumina, iron, etc., if the basic acetate method has been used, are evaporated down to a bulk of about 100 c.c., best in the platinum basin, after ammonia water has been added to alkaline reaction. This will in almost all cases produce a precipitate of aluminum and ferric hydroxides, which must be filtered off on a small filter, ignited and weighed. It is at this point that there is danger of neglecting to collect the slight precipitate of alumina, if the manganese is precipitated without previous filtration, so that any alumina or iron present is weighed with it.

The filtrate is caught in a 200-c.c. Erlenmeyer flask, and if the platinum basin is stained brown by deposited manganese, this is

[1] For an example see p. 243.

[2] Hillebrand, pp. 115–116.

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to be dissolved in a few drops of hydrochloric acid and a drop of sulphurous acid and washed into the flask.

Enough ammonia water is added to make the contents of the flask strongly alkaline, and a current of H_2S is passed through it for ten minutes, which precipitates the manganese, and also nickel, cobalt, copper and zinc, and the platinum which may have been derived from the basin. The flask is corked and allowed to stand for twenty-four hours.

The precipitated sulphides are collected on a 7-cm. filter, and washed with water containing a little ammonium chloride and ammonium sulphide, the flask being also rinsed out with this. The filtrate is received in a 400-c.c. beaker, and reserved for the determination of lime and magnesia (p. 177).

The sulphide of manganese (and zinc) is dissolved by passing a few cubic centimeters of hydrogen-sulphide water acidified with one-fifth of its bulk of hydrochloric acid through the filter, and the filter is washed several times. The liquid is received in a small porcelain or platinum basin and evaporated to dryness. A few drops of solution of sodium carbonate are added and the contents of the dish are again evaporated to destroy ammonium salts, which would hinder the complete precipitation of manganese. The dry salts are then dissolved in about 10 c.c. of water to which a few drops of hydrochloric acid are added, and are precipitated with sodium carbonate. The manganese carbonate is collected on a $5\frac{1}{2}$-cm. filter, washed, ignited in a weighed crucible and weighed as Mn_3O_4.

The black residue on the filter may contain nickel, cobalt, copper and platinum. The filter is incinerated in a porcelain crucible, and the residue is dissolved in a few drops of aqua regia, evaporated to dryness in the crucible, dissolved in a little water and hydrochloric acid, and a little strong hydrogen-sulphide water is added, which will precipitate the copper and platinum. These are filtered off on a small filter, and in the filtrate, to which ammonia is added, nickel and cobalt are precipitated by hydrogen sulphide. A few drops of acetic acid are added and the liquid is allowed to stand for some hours, when the nickel (and cobalt) sulphides are caught on a $5\frac{1}{2}$-cm. filter, ignited and weighed as oxide. The amount of cobalt is so small in terrestrial rocks that it is not necessary to separate it from the nickel, but its presence

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may be established, if desired, by testing the oxide with the borax bead.

It is, however, almost always best to determine nickel and copper in a separate portion, as described on p. 238.

18. Total Sulphur, Zirconia, Baryta, and Rare Earths

These constituents may be determined in separate portions, but it will be found to be a great economy of time to determine them in the same portion by the following plan, which was first published by Hillebrand,[1] and independently worked out by myself. The whole process, while apparently complicated, in reality takes very little extra time for its execution, as the volumes of liquid are small, and the various operations may be carried out during pauses between the main determinations, when solutions are being evaporated, etc.

Decomposition.—For this set of determinations 1 gram of rock powder is sufficient.[2] About this amount is weighed out into a weighed platinum crucible, mixed with four or five times its weight of sodium carbonate, and the mixture is fused precisely as has been described above (p. 131).

If pyrite is present, and it is desired to determine the sulphur, a small quantity, about ¼ gram, of powdered potassium nitrate is mixed with the carbonates, which should have been tested to see if they are free from sulphur or sulphates. If much niter is used the crucible is liable to be attacked. The reaction between the nitrate and the carbonates gives rise to considerable effervescence, and the fusion should, therefore, be carried on cautiously, and at as low a temperature as possible, till all nitrous fumes have disappeared. The temperature may then be raised and the operation carried on as above.

When the cake is perfectly cold it is detached from the crucible and thoroughly leached with water, till all soluble matter is dissolved, a drop or two of alcohol being added to reduce any sodium manganate which may be present.

[1] Hillebrand, p. 138.

[2] If the rare earths are to be looked for, 2 grams should be taken. In this case 8 grams of sodium carbonate are used for the fusion.

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Of the constituents which immediately concern us, the sulphur (that as sulphide as well as that as sulphate) passes into solution as sodium sulphate, while the baryta and zirconia remain undissolved, the former as barium carbonate and the latter as sodium zirconate. The rare earths are also insoluble.

Sulphur.—The liquid is filtered through a 7-cm. filter, as little as possible of the undissolved residue being brought on this, and the residue and filter are well washed with a very dilute solution of sodium carbonate to prevent turbid washings (Hillebrand). The further treatment of the residue will be found below under Zirconia.

If the filtrate is yellow the presence of chromium is indicated and this may be determined either in this liquid, or in a separate portion, by the colorimetric method, as described on p. 237. In most rocks the filtrate is colorless, when the absence of chromium may be noted in the tabulation of the analysis, and this constituent need not be looked for. Assuming that it is absent, or even when it is present,[1] we may proceed to the determination of the sulphur in this liquid.

The filtrate, which should amount to from 150–250 c.c. in a 400-c.c. beaker, is colored with two or three drops of methyl-orange solution, and hydrochloric acid is added gradually through a small funnel with curved tip, the beaker being covered to prevent loss, till the original orange color changes to pink, indicating that the liquid is acid. About half or, at most, 1 gram of barium chloride dissolved in 25 c.c. of water is added to the boiling liquid, the cover and sides washed down, and the beaker allowed to stand till the barium sulphate has settled. There is little danger of silica contaminating the barium sulphate, in the bulk of liquid recommended above, but if this should happen it is removed later. It is obvious that failure of barium chloride to produce a precipitate indicates the absence not only of S, but of SO_3. In this case this last need not be looked for, but both may be stated in the tabulation as absent.

The liquid is filtered, all the barium sulphate being brought on a small filter (7 cm.) by means of a rubber-tipped rod and the

[1] The free hydrochloric acid present prevents the precipitation of barium chromate. The colorimetric determination of chromium, if it is done here, should precede the determination of sulphur.

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wash-bottle; the filter is now well washed. The filter is ignited in a small weighed crucible, the barium sulphate evaporated with a few drops of hydrofluoric and one of sulphuric acids to expel any silica possibly present, again ignited and weighed. Further purification of the barium sulphate is seldom necessary.

For the very small amounts of sulphur present in most igneous rocks the precautions and refinements that have been suggested [1] in the precipitation of barium sulphate, to insure its purity, are not necessary.

If no sulphur trioxide is present in the rock, the weight of barium sulphate is multiplied by 0.137 to reduce it to S. If sulphur trioxide is present, the weight of barium sulphate is multiplied by 0.343 to reduce it to SO_3, which is changed to percentage figures by division by the weight of substance taken. From this the percentage of sulphur trioxide present in the rock as obtained in a separate portion (p. 231) is deducted, and the remainder multiplied by 0.401 to reduce the SO_3 to S.

Zirconia.—The whole of this is present as sodium zirconate in the residue insoluble in water. The small part of this which adheres to the filter is washed back into the beaker containing the bulk of the residue, by holding the funnel sidewise and directing a strong stream of water from the wash-bottle against all parts of the filter, the liquid dropping into the beaker beneath. With care, and if done while the residue is still moist, the removal can easily be made complete. It is of no consequence if a little remains on the filter.

To the contents of the beaker, the bulk of which should be less than 50 c.c., not more than three or four drops of concentrated sulphuric acid are added. A larger amount is to be avoided, as too much free sulphuric acid prevents the entire precipitation of the zirconia (Hillebrand), and also retards filtration through action on the filter-paper. The liquid is warmed (not boiled) till all effervescence ceases, and another drop or two of sulphuric acid is added to see if solution has been complete. The liquid should be distinctly acid. The liquid is filtered through the original filter into a flask of about 100 c.c., and the filter and beaker are washed several times with small quantities of warm water.

[1] Allen and Johnston, Jour. Am. Chem. Soc., **32**, p. 588, 1910; Johnston and Adams, op. cit., **33**, p. 830, 1911.

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The filtrate now contains all the zirconia as sulphate, while the baryta remains behind as insoluble barium sulphate, along with strontia and some lime and silica. For the treatment of this insoluble portion, see p. 229.

To the filtrate in the flask is now added about 5 c.c. of hydrogen peroxide, or enough to cause a permanent yellow coloration, and then 1 c.c. of a solution of a soluble phosphate, such as microcosmic salt. The flask is filled nearly to the neck, if not so already and set aside in a cool place for at least twenty-four hours, and preferably for twice that length of time. If the yellow color disappears, a little more hydrogen peroxide is to be added.

The zirconia separates as a flocculent precipitate of basic zirconium phosphate, which may easily be overlooked unless the flask is gently agitated. It is almost or entirely free from titanium the precipitation of which is prevented by the hydrogen peroxide. However small the precipitate may appear it is filtered off through a $5\frac{1}{2}$-cm. filter, and well washed. The filtrate is reserved for the determination of the rare earths, if these are to be looked for (p. 229).

For most rocks, in which the amount of ZrO_2 is very small, further purification is unnecessary, and the filter and precipitate are ignited in a small weighed crucibile, and weighed as basic zirconium phosphate. This contains 51.8 per cent of ZrO_2, but for the minute quantities usually present it will suffice to multiply it by 0.5 to reduce it to ZrO_2. The percentage amount of ZrO_2 is to be subtracted from that of the ignited precipitate by ammonia to arrive at the correct figure for alumina.

If the precipitate is large, or if extreme accuracy is desired, the purification recommended in every case by Hillebrand may be carried out. The ignited precipitate (unweighed) is fused with a very little sodium carbonate, leached with water and filtered. The small filter and contents are ignited and then fused with a small lump of acid potassium sulphate. The cooled melt is dissolved in hot water and a drop or two of dilute sulphuric acid. To the solution in the crucible a little hydrogen peroxide and a few drops of soluble phosphate are added, and the covered crucible is set aside as before. The precipitated zirconium phosphate now free from titanium, is collected, ignited and weighed as above. For identification of the zirconia the reader is referred to Hillebrand.

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Baryta.—The residue left on solution of the zirconia in dilute sulphuric acid contains all the baryta, with traces of strontia and often much lime, as insoluble sulphates. To bring these into solution it is collected on a small filter, as described above, the filter and contents are ignited in a small crucible and fused with about 1 gram of sodium carbonate, the fusion being continued for ten to fifteen minutes to permit the complete conversion of the barium sulphate into carbonate. There should be enough carbonate for this conversion by mass action.

The cake is leached with warm water, which may be done in the crucible, filtered through a small filter, and well washed. After a fresh 250-c.c. beaker has been placed beneath the funnel, the carbonates are dissolved on the filter in a very little, warm, dilute hydrochloric acid, and the filter is well washed. The liquid in the beaker is made up to at least 150 c.c. to prevent precipitation of strontium and calcium sulphates, and 2 or 3 c.c. of concentrated sulphuric acid are added. After standing for twenty-four hours, the precipitated barium sulphate is filtered off, ignited, and weighed. It will seldom be necessary to purify it for contamination by calcium or strontium. Multiplication of the weight of $BaSO_4$ by 0.66 reduces it to BaO.

Rare Earths.—It may be desired to determine the so-called rare earths, oxides of the metals of the cerium and yttrium groups, as appreciable amounts of these may be present in highly sodic rocks (p. 18). This may be done by a simple method devised by Hillebrand,[1] which is quite accurate enough for the very small amounts that are ever found in rocks. If the total percentage of rare earths amounts to several tenths of a per cent it may be well to separate them into the earths of the cerium and yttrium groups.

For the determination of the rare earths it is most convenient to use the acid filtrate from the precipitate of zirconium phosphate, inasmuch as zirconium should always be determined if the composition of the rock warrants the search for the rare earths, because both are found together in relatively largest (though usually absolutely small) amounts in highly sodic rocks.[2]

[1] Hillebrand, p. 143; M. Dittrich, Berichte, **41**, p. 4373, 1908; J. Morozewicz, Bull. Ac. Sci., Crac., 1909, p. 207.

[2] Cf. H. S. Washington, Trans. Am. Inst. Min. Eng., 1908, p. 755.

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The filtrate from the zirconium phosphate is precipitated with a solution of potassium or sodium hydroxide in decided but not too great an excess. This will keep the alumina in solution but will precipitate the rare earths along with the ferric oxide and titanium dioxide. The precipitate is washed several times with hot water, brought on a 9- or 11-cm. filter where it is again washed twice or thrice.

It is then washed by a jet from the wash-bottle into a small platinum basin, a few cubic centimeters of hydrofluoric acid are added, enough to just dissolve the precipitate, and the liquid is evaporated to dryness. No sulphuric acid is added. The soluble fluorides, of iron and possibly titanium, are dissolved in a little water containing a few drops of hydrofluoric acid, and the insoluble rare earth fluorides are collected in a $5\frac{1}{2}$-cm. filter, supported in a small rubber funnel. In these operations only platinum vessels can be used, as glass or porcelain would be attacked by the hydrofluoric acid.

The washed filter and contents are ignited in a platinum crucible, a few cubic centimeters of dilute sulphuric acid added, and the contents are evaporated to dryness. The small mass is taken up with a little dilute hydrochloric acid, transferred to a small beaker and the rare earths are precipitated as hydroxides with a slight excess of ammonia water. The hydroxides are slightly washed and then dissolved on the filter in a little dilute hydrochloric acid, and precipitated with a decided excess of concentrated solution of ammonium oxalate. The oxalate is collected on a $5\frac{1}{2}$-cm. filter, washed with water containing a little of this salt, ignited and weighed in a platinum crucible, as $(Ce,Y)_2O_3$.

If the weight is more than a few milligrams the earths of the two main groups may be separated by dissolving the oxides in a very small volume of dilute hydrochloric acid, evaporating down almost to crystallization, adding a few drops of water, and, finally, a few cubic centimeters of cold concentrated solution of normal potassium sulphate. This should have been prepared beforehand, and must contain some undissolved potassium sulphate crystals. On standing, a double sulphate of potassium and cerium separates, as this is almost insoluble in the potassium sulphate solution, whereas the double sulphates of the metals of the yttrium group are easily soluble in it. The precipitate is fil-

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tered off in a small filter, washed with the concentrated potassium sulphate solution, dissolved in dilute hydrochloric acid, precipitated with ammonia water, and the precipitate is ignited and weighed. The ignited oxide is the dioxide of cerium, CeO_2, of a peculiar dark, reddish brown color. This may be calculated into the sesquioxide, Ce_2O_3, in which form the rare earths are stated in the analysis, by multiplying the weight by the factor 0.95, but the weight is usually so small as to make this an ultra-refinement.

The earths of the yttrium group may be determined by difference from the weight of the mixed oxides, or may be precipitated as hydroxides, ignited and weighed as Y_2O_3. Further separation of the elements of the two groups is neither called for nor usually practicable. The weight of the rare earths is to be subtracted from that of the alumina precipitate.

19. Sulphur Trioxide [1]

Sulphur trioxide, which is present usually in haüyne and noselite, both soluble in hydrochloric acid, is determined in a separate portion. About 1 gram is weighed out (p. 129) into a 250-c.c. beaker, and gently boiled with 50 c.c. of dilute hydrochloric acid (1 : 5). If pyrite or pyrrhotite are present, a stream of carbon dioxide should enter by the lip of the covered beaker, and fill the space beneath the cover before boiling is begun. It is, of course, continued during the boiling. In this way any pyrite remains unattacked, while seven-eighths of the sulphur of pyrrhotite goes off as hydrogen sulphide, the remaining one-eighth being precipitated as sulphur. This need not be filtered off, as it is burned in the subsequent ignition.

After boiling for about a quarter of an hour, the liquid is filtered through a 9-cm. filter, and the residue and filter are washed. The volume of liquid should be about 200 c.c., to prevent precipitation of silica. It is then precipitated, best while hot, with an excess of barium-chloride solution, allowed to stand for some time and the barium sulphate is filtered off, well washed, ignited and weighed. To guard against contamination by silica it is always as well to evaporate the ignited precipitate with a few

[1] Hillebrand, p. 199.

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drops of hydrofluoric and sulphuric acids, and again ignite. The weight of $BaSO_4$ is multiplied by 0.343 to obtain that of SO_3.

Before determining sulphur or sulphuric anhydride, the condition in which the sulphur exists in the rock should be investigated. The microscope will usually reveal the presence of pyrite or pyrrhotite, as well as noselite or haüyne. If not, the rock powder should be boiled with a little dilute hydrochloric acid, and if hydrogen sulphide is evolved the presence of pyrrhotite may be inferred, as the lazurite molecule is not apt to be found in rocks. A little of the filtered liquid may be tested with barium chloride for SO_3.

20. Chlorine [1]

While Hillebrand recommends fusion with chlorine-free sodium carbonate, to ensure getting all the chlorine, yet it is not only difficult to procure such a reagent, but the operation will be somewhat long and complex. For nearly all purposes simple solution in nitric acid, if desired with the addition of some hydrofluoric acid, will be quite sufficient.

About 1 gram of rock powder is weighed out into a 250-c.c. beaker and boiled with 50 c.c. of dilute nitric acid (1 : 5) which should have been previously tested as to freedom from chlorine; or a blank determination is to be made with the same volume of the acid to allow of a suitable correction if chlorine-free acid is unobtainable. If the addition of hydrofluoric acid is desired the digestion should be carried out in a capacious crucible or small platinum basin.

After heating gently on the water bath for a quarter of an hour, the liquid is filtered,[2] the filter and residue are well washed and the filtrate is precipitated with excess of silver nitrate solution. It is heated with constant stirring, to coagulate the silver chloride. If the precipitate is at all considerable, it is filtered through a small filter and, after washing, is dissolved on the filter with ammonia water, reprecipitated by acidifying with nitric acid to free it from possibly contaminating silica, and

[1] Hillebrand, p. 183.

[2] A rubber or platinum funnel and the platinum basin are to be used if hydrofluoric acid has been added.

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collected in a weighed Gooch crucible. After washing, it is dried, heated to incipient fusion and weighed. The weight of the AgCl multiplied by 0.247, or 0.25 for small amounts, will give the weight of chlorine present.

If the precipitate is very small, Hillebrand recommends that it be collected on a small paper filter, which is then dried, wound up in a weighed platinum wire and carefully ignited. The increased weight of the wire is due to the metallic silver of the chloride which has alloyed with the platinum, and is multiplied by 0.33 to arrive at the chlorine.

If the chlorine is present only in minerals of the sodalite group, solution in nitric acid alone will usually be sufficient. But if scapolites are present, some of which are not attacked by this acid, the addition of hydrofluoric acid will be necessary.

In the determination of chlorine the reagents used must be free from chlorine, and a duplicate operation in blank with the same quantities will be a wise precaution. Rock specimens collected near the seashore are sometimes contaminated with sodium chloride derived from sea-water. This may be estimated in a separate portion by thorough washing on a filter with warm water, and determination of the chlorine dissolved out. This is, of course, to be deducted from the amount of chlorine which is found by the previous method, and its equivalent amount of Na_2O from that of this constituent already found.

21. Fluorine [1]

It is only in very exceptional rocks that fluorine occurs in more than one or two-tenths of 1 per cent. As it is usually present only as a constituent of apatite, its amount may be calculated from that of the phosphorus pentoxide present with sufficient accuracy for most purposes. The methods for its determination are somewhat tedious, and, as it is of apparently small import in theoretical petrology, the determination of fluorine may generally be dispensed with.

It may be determined either gravimetrically or colorimetrically. Of the former the old method of Berzelius may be used, with modifications proposed by Penfield and Minor.[2]

[1] Hillebrand, pp. 184–193; Mellor, pp. 637–640.

[2] Penfield and Minor, Am. Jour. Sci., **47**, p. 388, 1894.

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About 2 grams of the rock powder are fused with five times its weight of alkali carbonates, and the cake is thoroughly leached with hot water, filtered and washed. The filtrate contains all the fluorine as alkali fluorides. While still hot about 5 grams of powdered ammonium carbonate are added to the filtrate, and when cold about the same amount is again added. The beaker is allowed to stand for about twelve hours, the precipitate is filtered off and washed, and the ammonium carbonate in the filtrate is decomposed by heating on the water-bath till no more carbon dioxide is given off. About 5 c.c. of a solution of zinc oxide in strong ammonia water is added and the liquid is evaporated till there is no more odor of ammonia. After filtering off the precipitate and washing, nitric acid is added to the filtrate till the alkali carbonate is nearly, but not entirely, decomposed. If too much is added, a solution of sodium carbonate is poured in to a decided alkaline reaction.

As chromic and phosphoric acids may be present, Hillebrand recommends the addition at this point of silver nitrate in excess, which will precipitate these substances. The liquid is heated and filtered, the excess of silver precipitated by sodium chloride, again heated to coagulation and again filtered, when a little sodium carbonate is added to alkaline reaction. If no chromium or phosphorus is present, or only small amounts, the addition of silver nitrate may be dispensed with.

The heated filtrate, which contains alkali carbonate and fluoride, and which must not contain ammonium salts, is now precipitated with an excess of calcium chloride. The precipitate of calcium carbonate and fluoride is collected on a filter, placed in a weighed platinum crucible, dried and ignited gently. A little water and 1 or 2 c.c. of acetic acid are poured in, and the covered crucible is heated for some time on the water-bath, and finally the excess of acid is evaporated with the cover off of the crucible.

Hot water is poured on the dry salts, and the contents of the crucible are filtered through a small filter and washed. The filter with its contents are again ignited in the same crucible, and the digestion with dilute acetic acid and evaporation are gone through with again. The ignition of the filters and the digestion with dilute acetic acid are repeated till all the calcium carbonate and oxide are dissolved as acetate, as is shown by the absence of a

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residue on evaporation of a few drops of the filtrate on platinum foil.[1]

The filter and purified calcium fluoride are finally gently ignited in the crucible and weighed. Multiplication of the weight of CaF_2 by 0.49, or division by 2 in most cases, gives the amount of fluorine. For possible corrections see Hillebrand.

A colorimetric method of determining the small amounts of fluorine found in rocks, based on the bleaching effect of fluorine on hydrogen peroxide solutions of titanium, has been proposed by G. Steiger.[2] The method in brief consists in fusing the rock with sodium carbonate, leaching with water, and mixing a definite amount of standard titanium solution with the filtrate, which is compared colorimetrically with a fluorine-free titanium solution. The percentage of fluorine is shown by reference to a curve which has been determined empirically, and for this and other details the student is referred to the original paper or to Hillebrand.

Steiger's method has been modified by Merwin,[3] who also gives the curves determined from his empirical data. For this method the student would best consult Merwin's paper, the portion of the paper relating to the fluorine determination is also given by Hillebrand (pp. 191–193).

These methods, which are only adapted to small amounts of fluorine, may be recommended for use in rock analysis for their rapidity, simplicity, and greater accuracy than the usual gravimetric methods. It may, however, be repeated that it is seldom worth while to determine fluorine in rocks.

22. Carbon Dioxide[4]

As all the minerals which contain this constituent are soluble in hydrochloric or nitric acid with evolution of carbon dioxide (dolomite and siderite only on warming), its qualitative presence may be easily established by warming the rock powder with a

[1] Penfield and Minor show that the addition of acetic acid in large amount at a time leads to loss of calcium fluoride.

[2] G. Steiger, Jour. Am. Chem. Soc., **30**, p. 219, 1908; Hillebrand, pp. 188–193.

[3] H. E. Merwin, Am. Jour. Sci., **28**, p. 124, 1909.

[4] Classen, **2**, pp. 653–656; Fresenius, **1**, pp. 493–495; Hillebrand, pp. 179–181; Mellor, pp. 553–555; Treadwell, **2**, pp. 380–382.

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little, somewhat dilute nitric or hydrochloric acid, and noting whether effervescence ensues. This is done in a test-tube. If there is no marked effervescence, one may make sure of the reaction, as Hillebrand suggests, by inclining the tube and examining the upper side with a lens for the stream of minute bubbles. Before the addition of the acid the powder should be well stirred up with warm water to drive out any mechanically attached air, bubbles of which might be mistaken for CO_2. If the rock contains considerable pyrrhotite, the evolution of hydrogen sulphide may be mistaken for that of carbon dioxide, but the former is easily recognizable by its characteristic odor, as well as by the blackening of paper soaked in lead acetate solution to which a drop of ammonia has been added.

The determination of carbon dioxide is effected by the usual method, which is so well-known that a brief description will suffice. Any of the well-known forms of apparatus may be used, and if many determinations are to be made it will be as well to have one permanently set up.

At least 2 or 3 grams of rock powder are weighed out into a small flask. After mixing the powder with some water, the flask is connected on one side with a cylinder filled with soda-lime or sticks of caustic alkali, to free the air from CO_2. On the other side it is connected with an upward inclined condenser, then a U-tube containing glass beads wet with concentrated sulphuric acid, which may be designated as *a*. Tube *a* is followed by U-tubes *b*, *c*, *d*, *e*, *f*, and *g* in the order given. Tube *b* contains granular, anhydrous calcium chloride; *c* contains pieces of pumice which have been soaked in a copper sulphate solution and heated at 150° for several hours. At this temperature the calcium sulphate is partly dehydrated and easily retains both the H_2S and HCl which may escape from the flask. Tube *d* contains granular, anhydrous calcium chloride; *e* contains soda-lime and *f* contains soda-lime in the arm nearest *e* and granular anhydrous calcium chloride in the other arm. Tubes *e* and *f* are the absorption tubes, both of which must be weighed carefully. Tube *g* contains calcium chloride in the arm nearest *f* and soda-lime in the other arm.

After weighing the soda-lime U-tubes and connecting them in place, the whole apparatus is filled with dry and carbon-dioxide-

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free air by means of an aspirator attached to the last U-tube. About 10 c.c. of dilute hydrochloric acid are added to the flask containing the powder and its contents boiled gently while a slow current of air free from carbon dioxide is passing. In ten or fifteen minutes decomposition is complete. The flame is now removed and the current of air continued for some time longer in order to drive all CO_2 into the absorption tubes.

The U-tubes are then removed, carefully closed, and allowed to cool thoroughly, as the absorption of the carbon dioxide by the soda-lime gives rise to considerable heat. They are then weighed, the increase being the amount of CO_2 in the portion of rock powder taken.

A very simple and sufficiently accurate apparatus for the indirect determination of carbon dioxide by loss of weight has been described by Kreider.[1]

23. Chromium and Vanadium[2]

These constituents are so seldom present in appreciable amount in silicate igneous rocks that the analyst will not often be called on to determine them.

Chromium is occasionally to be determined in such rocks as dunites, peridotites, pyroxenites, etc., and for this the colorimetric method recommended by Hillebrand is to be used. It is briefly summarized here.

If the filtrate from the leached sodium carbonate melt for sulphur, baryta, and zirconia,[3] is yellow, this may be used for the chromium determination. It is evaporated down to a bulk of less than 100 c.c., and the chromium is determined as described below. The total sulphur may be determined afterwards in this solution by precipitation as barium sulphate (p. 225).

If it is desired to determine chromium in a separate portion, at least 2 grams of the rock powder are thoroughly fused with four times its weight of sodium carbonate, and the cake is extracted with water, as in the method for total sulphur (p. 225). A few drops of either ethyl or methyl alcohol are added to destroy the

[1] Am. Jour. Sci., **19**, p. 188, 1905; cf. Hillebrand, p. 181.
[2] Hillebrand, pp. 147–150; Mellor, pp. 472–474.
[3] See p. 225.

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color of sodium manganate, and the liquid is filtered. If the yellow color is very faint, or invisible, the liquid should be concentrated to small bulk for use as the test solution, and placed in a small measuring-flask of 25, 50 or 100 c.c., according to the depth of color, which must be less than that of the standard solution. This last is prepared by dissolving 0.25525 gram of normal potassium chromate (K_2CrO_4) in a liter of water, the solution containing then 0.0001 gram of Cr_2O_3 per cubic centimeter.

The depth of color of the test solution is then compared with that of the standard exactly as was done in the determination of titanium dioxide (p. 169) or manganese by the colorimetric method, a definite volume of standard being diluted with water from a burette till the two colors are alike. The results, as shown by Hillebrand, are very accurate for the small quantities found in rocks.

The determination of vanadium is so seldom necessary, and the method is so complex, that it need not be given here. If it is desired to determine it, Hillebrand's method should be used, a full description of which is given by him.[1]

It is to be remembered that the vanadium, as V_2O_5, is to be subtracted from the apparent percentage of P_2O_5, as it is precipitated with this as vanadomolybdate (p. 216).

Molybdenum may be determined in the portion used for vanadium. It is scarcely ever looked for but if it is desired to do so the method of Hillebrand[2] may be used.

24. Copper and Nickel[3]

If it is desired to determine copper, or other metals of the hydrogen-sulphide group, which may rarely be present, it is advisable to use a separate portion, rather than determine them in the sulphides remaining after determination of manganese in the main portion, if the acetate method has been used. This is chiefly because in this they are contaminated with platinum, and partly because appreciable amounts of copper will probably have been introduced from the water-baths (Hillebrand).

[1] Hillebrand, pp. 148–154.
[2] Ibid., p. 150.
[3] Cf. p. 18, 19; Hillebrand, pp. 98, 116, 220.

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The weighed portion, preferably about 2 grams, is decomposed in a platinum crucible (placed in the radiator described on p. 40) with sulphuric and hydrofluoric acids. When decomposition is complete, as indicated by the absence of gritty particles, the contents of the crucible are evaporated to dryness. Complete expulsion of the hydrofluoric acid is insured by adding sulphuric acid and again evaporating to dryness, repeating the operation, if necessary. The residue in the crucible is digested with dilute sulphuric acid (1:4) for about five minutes and after a second dilution (1:8) is filtered. Hydrogen sulphide is now passed into the filtrate.

The precipitated cupric sulphide is filtered off rapidly and washed with water containing hydrogen sulphide. The filter containing it is ignited in a small weighed platinum crucible, moistened with a few drops of nitric acid, cautiously evaporated to dryness, ignited, and the residue is weighed as CuO. Multiplication of this by 0.8 reduces it to Cu.

Ammonia in excess is added to the filtrate, and a current of hydrogen sulphide passed through it for a quarter of an hour, a few drops of acetic acid are added, and the liquid is allowed to stand for some hours, when the nickel (and cobalt) sulphides are caught on a 5½-cm. filter, ignited and weighed as oxide. The amount of cobalt in terrestrial rocks is so small that it is not necessary to separate it from the nickel, but its presence may be established, if desired, by testing the oxide with the borax bead.

Nickel may also be determined as nickel dimethyl glyoxime,[1] either in the original slightly acid solution of the rock powder if copper is not to be determined, or in the filtrate from the copper sulphide.

The slightly acid solution is almost neutralized with ammonia, about 2 grams of tartaric acid added to hold up iron, and a little acetic acid added. It is then heated nearly to boiling and about 5 or 10 c.c. of 1 per cent alcoholic solution of dimethyl glyoxime are added. The volume of the alcohol should be less than half that of the solution containing the nickel, because of the slight solubility of the precipitate in alcohol. Ammonia water is added drop by drop, with stirring, until the liquid smells slightly of it, and the voluminous reddish precipitate is filtered hot through a

[1] Treadwell, **2**, pp. 129–130.

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weighed Gooch crucible. It is washed with hot water, dried at 110°, and weighed. The weight of the precipitate, which has the composition $Ni(C_4H_7N_2O_2)_2$, is multiplied by the factor 0.259 to reduce it to NiO.

25. Boric Oxide [1]

Boric oxide is seldom, if ever, determined in rocks, though it occurs in tourmaline-bearing granites and in metamorphic rocks that contain axinite or dumortierite. This neglect has been due chiefly to the difficulties connected with its exact determination. As, however, it may be of interest to determine it in some rocks, as well as in glasses, which are essentially silicate material, a brief description of a reliable method will be given here.

Chapin found that, with some modifications, the Gooch-Rosenblaadt method could be adapted to the analysis of minerals containing boric oxide; and Allen and Zies find that Chapin's method is by far the most trustworthy for determining the boric oxide content of glasses, so that, therefore, it should be applicable to rocks, which are of less complex composition than many glasses. For the details Chapin's and Allen and Zies' papers should be consulted.

The rock powder is fused with sodium carbonate and the cake is brought into solution with hydrochloric acid, exactly as with the main portion (pp. 131 et seq.), except that the amount of acid is kept as small as possible. After dehydration of the unfiltered liquid by the addition of calcium chloride, the boric oxide, freed by the hydrochloric acid, is volatilized as methyl borate by passing the vapor of specially pure methyl alcohol through the hot liquid and is collected by distillation. The solution of methyl borate in methyl alcohol so obtained is treated with an excess of sodium hydroxide to form sodium borate, from which the alcohol is distilled off without loss of boric oxide. The excess of sodium hydroxide is then titrated with hydrochloric acid, and finally the free boric oxide is titrated with barium hydroxide in the presence of mannite.

[1] Hillebrand, pp. 199–200; Mellor, pp. 578–589; Gooch, Am. Chem. Jour., **9**, p. 23, 1887; T. Rosenblaadt, Zeits. Anal. Chem., **26**, p. 21, 1887; W. H. Chapin, Jour. Am. Chem. Soc., **30**, p. 1691, 1908; Allen and Zies, paper to be published in the Jour. Am. Ceram. Soc., I am indebted to Dr. Zies for this sketch of the Chapin method, which he has used in the study of optical glasses in this laboratory.

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APPENDIXES

1. Factors for Calculation

Constituent.	Sought.	Found.	Factor.	Logarithm.
Baryta	BaO	$BaSO_4$	0.66	9.81954
Chlorine	Cl_2	$AgCl$	0.247	9.39270
Chlorine	Cl_2	Ag	0.33	9.51851
Copper	Cu	CuO	0.80	9.90309
Fluorine	F_2	CaF_2	0.49	9.69020
Magnesia	MgO	$Mg_2P_2O_7$	0.3621	9.55883
Manganous oxide	MnO	Mn_3O_4	0.93	9.96848
Manganous oxide	Mn_3O_4	MnO	1.08	0.03342
Phosphorus pentoxide	P_2O_5	$Mg_2P_2O_7$	0.638	9.80482
Phosphorus pentoxide	P_2O_5	$24MoO_3 \cdot P_2O_5$	0.04	8.60206
Potash	K_2O	K_2PtCl_6	0.1934	9.28646
Potash	KCl	K_2PtCl_6	0.307	9.48714
Potash	K_2O	$KClO_4$	0.3393	9.53058
Potash	KCl	$KClO_4$	0.538	9.73078
Soda	Na_2O	$NaCl$	0.5304	9.72460
Strontia	SrO	$SrSO_4$	0.56	9.74819
Sulphur	S	$BaSO_4$	0.137	9.13672
Sulphur trioxide	SO_3	$BaSO_4$	0.343	9.53529
Zirconia	ZrO_2	$xZrO_2 \cdot yP_2O_5$	0.52	9.71600

To obtain the weight of the substance sought, the weight of the substance found is multiplied by the appropriate factor. The factors are based on the 1916 Table of Atomic Weights,[1] and are carried out only as far as is deemed appropriate for the quantities usually found in igneous rocks.

[1] Clarke, Thorpe, and Urbain, Jour. Am. Chem. Soc., **38**, p. 2220, 1916. For a discussion of appropriate atomic weights to be used in factors, see Mellor, p. 250.

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2. Example of Analysis

The rock analyzed is a gray porphyritic basaltic lava from Mt. Etna showing in the hand specimen conspicuous augite and olivine phenocrysts about 5 mm. in diameter, and less conspicuous but more numerous crystals of plagioclase. Microscopically the plagioclase is found to be about Ab_2An_3 to Ab_1An_2. The same minerals are represented in the holocrystalline groundmass together with necessary magnetite and apatite.

The frontispiece is from a drawing representing the summit of Mt. Etna about 100 years after this lava was extruded.

There are given the partial results of an analysis that was made to check up the times taken for the various determinations and operations. The analysis was begun on June 12, at 8:30 A.M. and the determinations given here were completed by noon of June 16, though there were several interruptions. The working day was from 9 A.M. to 4:30 P.M. The calculations are presented in common arithmetical form, though (five-place) logarithms may be used, and will save time and space.

The results of the complete analysis are as follows:

BASALT. LAVA OF 1669. CATANIA, MT. ETNA

SiO_2	49.62
Al_2O_3	16.00
Fe_2O_3	2.81
FeO	7.61
MgO	5.20
CaO	10.25
Na_2O	4.12
K_2O	1.46
H_2O+	0.22
H_2O-	0.07
CO_2 [1]	none
TiO_2	1.64
ZrO_2 [1]	none
P_2O_5	0.62
S [1]	0.05
Cr_2O_3 [1]	none
MnO	0.13
BaO [1]	0.09
SrO	0.03
	99.92

[1] These determinations are not given in the example.

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E, 10. BASALT. LAVA OF 1669. CATANIA, MT. ETNA

SiO_2, H_2O+, H_2O-, MnO.

Cruc.+subst. =33.0909
Cruc. (palau) =32.0712
Main portion [1] = 1.0197

SiO_2, 49.62

Cruc.+SiO_2+x=25.0185
Cruc. =24.5101
.5084

Cruc.+SiO_2+x =25.0185
Cruc.+x =24.5159
Main SiO_2 = .5026
Extra SiO_2 = .0034

1.0197).50600(.4962
40788
98120
91773
63470
61182
22880

Cruc.+extra SiO_2+x=24.5176
Cruc.+x =24.5142
Extra SiO_2 [2] = .0034

H_2O+, 0.22

Tube+subst. =28.7643
Tube =28.2492
Subst. taken = .5151

Tube+H_2O =21.1212
Tube−H_2O =21.1197

.515).001500(.0029
1030
4700
4635

Total H_2O =0.29
H_2O- =0.07
H_2O+ =0.22

H_2O-, 0.07

Cruc.+subst. =33.2811
Cruc. =32.0700
1.2111

Cruc.+subst. =33.2811
Dried at 110° =33.2802

1.21).000900(.0007
847
53

Same portion, test solution diluted to 200 c.c.

MnO, 0.13

$\frac{1}{10}$ MnO, H_2O

10 cc. 15.8
16.3
16.0
3)48.1
10+16.03=26.03

26.03).00020000(.000007683
18221
17790
15618
21720
20824
8960
7809

200
.001536600

1.21).0015366(.0013
121
326

[1] The cold cake was almost colorless, with brown patches of iron carbonate, showing that very little manganese was present.

[2] This is the SiO_2 recovered from the alumina precipitate; see next page.

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E. 10. Al_2O_3, Fe_2O_3, TiO_2,

Cruc. + Al_2O_3 + etc.[1] = 24.8161
Cruc. = 24.5101
.3060

Al_2O_3, 16.00

Burette + $KMnO_4$ = 178.14
Burette − $KMnO_4$ = 131.73
46.41

Fe_2O_3, 2.81

Fe_2O_3 value [2] = .002473
46.41
2473
9892
14838
9892
Total Fe_2O_3 = .11477193
FeO as Fe_2O_3 [3] = .08616465

1.0197).02860728(.02805+
20394
82132
81576
55600
50985
4615

Al_2O_3, etc. = .3060
Fe_2O_3 = .1148
.1912
TiO_2 .0167
.1745
SiO_2 .0034
.1711
P_2O_5 .0063
.1648
Ash .0003
.1645
Mn_3O_4 .0013
1.0197).16320(.1600
10197
61230
61182
4800

Sol. from Fe_2O_3, test solution diluted to 500 c.c.

TiO_2. 1.64

$\frac{1}{10}$ TiO_2, 10 cc.

H_2O
11.8
12.5
12.1
3)36.4
10+12.13=22.13

1.0197).0167195(.01639
10197
65225
61182
40430
30591
98390

22.13).00074000(.000033439
6639
7610
6639
9710
8852
8580
6639
19410
19917

500
.0167195

[1] A little persulphate was added before precipitation with ammonia to throw down the manganese with the alumina, though this would generally not be necessary with the very small amount of manganese present.

[2] One gram of the permanganate solution = .002473 gram Fe_2O_3 or .002228 gram FeO.

[3] For the calculation of this see p. 245.

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E. 10. CaO, SrO, MgO, FeO,

CaO, 10.25

Cruc. + (Ca, Sr)O = 19.8538
Cruc. = 19.7490
(Ca, Sr)O = .1048

1.0197).104800(.1028
10197
28300
20394
79060

(Ca, Sr)O = 10.28%
SrO = .03 / 10.25

Cruc. + $SrSO_4$ = 19.7495
Cruc. = 19.7490
$SrSO_4$ = .0005
.56
.30
25
SrO = .000280

SrO, 0.03

MgO, 5.20

Cruc. + $Mg_2P_2O_7$ = 24.2078
Cruc. = 24.0614
$Mg_2P_2O_7$ = .1464

.3621
.1464
14484
21726
14484
3621

1.0197).05301144(.05198
50985
0264
10197
100670
91773
88970

FeO, 7.61

Cruc. + subst. = 32.5919
Cruc. = 32.0700
.5219

.002228[1]
17.83
6684
17824
15596
2228

.5219).03972524(.0761

Burette + $KMnO_4$ = 176.94
Burette − $KMnO_4$ = 159.11
17.83

.002473[2]
17.83
7419
19784
17311
2473

.5219).04409359(.0845

1.0197[3]
.0845
50985
40788
81576
.08616465

[1] The calculation of the FeO value of the permanganate.
[2] The calculation of the Fe_2O_3 value of the permanganate.
[3] The calculation of the FeO as Fe_2O_3 in terms of percentage of the main portion, for subtraction from the total iron oxides (p. 244).

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E. 10. ALKALIES, P_2O_5.[1]

K_2O, 1.46

Tube + subst. = 23.1212
Tube − subst. = 22.5639
.5573

Gooch + K_2PtCl_6 = 23.1475
Gooch = 23.1054
K_2PtCl_6 = .0421

Cruc. + NaCl + KCl = 30.0955
Cruc. = 30.0393
.0562[2]

NaCl + KCl = .0562
KCl = .0129
NaCl = .0433

Na_2O, 4 12

.1934 × .0421 = 7736 + 1934 + 3868 = .0129247

.5573) .00814214 (.0146
5573
25691
22292
33990

.5304 × .0433 = 21216 + 15912 + 15912 = .02296632

.5573) .02296632 (.0412
22292
6743
5573
11700

P_2O_5, 0.62

Pt. basin + subst. = 22.3397
Pt. basin = 21.1965
1.1432

Cruc. + $Mg_2P_2O_7$ = 24.0725
Cruc. = 24.0614
.0111

.0111 × .638 = 888 + 333 + 666 = .007081

1.143) .007081 (.0062
6858
2238

[1] On this page can also be recorded the data for BaO, S, and ZrO_2, which are omitted here.

[2] The weight of the mixed chlorides is very nearly the combined percentages of Na_2O and K_2O (p. 84); the presence of potassium chloride, with the higher atomic weight of potassium, tends to make up for the weight of substance taken being more than .5304 gram.

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3. References

The following works have been consulted and some of them are often cited.[1] In the references, as a general rule, only the author's name and page number are given.

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Gooch, F. A., Representative Procedures in Quantitative Chemical Analysis. New York, 1916, 262 pp. This book describes many of the analytical operations in considerable detail. About one-half of it is devoted to volumetric analysis, and the analysis of silicates is treated very inadequately.

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[1] For a fuller list see Mellor, p. 733.

[2] No. 176, 1900; No. 305, 1907.

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MELLOR, J. W., A Treatise on Quantitative Inorganic Analysis. London, 1913, 778 pp. This excellent work is replete with references, descriptions of alternative methods, and useful hints and tables. It is devoted largely to the analysis of silicates, including glazes, and will be found very useful to every analyst as a handbook for reference.

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TREADWELL, F. P., Analytical Chemistry; Vol. I, Qualitative Analysis, Vol. II, Quantitative Analysis. Translation by W. T. Hall, New York, 1916 and 1911. This well-known and very useful work, much superior to Fresenius, contains many recent methods, and should be in the hands of every analyst, though, like many others, its treatment of silicate analysis is too brief and little-detailed to be very serviceable to the student who is working alone.

WASHINGTON, H. S., Chemical Analyses of Igneous Rocks. U. S. Geological Survey Professional Paper 99. Washington, 1917, 1201 pp. This collection of chemical analyses of rocks is accompanied by a text, in which are discussed such topics as the character of rock analyses, including their accuracy, completeness, and representativeness, and the criteria by which to judge of their quality. It also includes a description of the quantitative classification of igneous rocks and the methods used in calculating the mineral composition. The large number of analyses recorded will give the student many examples of excellence to be emulated, as well as many "horrible examples" that show to what depths the careless and incompetent analyst can descend.

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